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INDUSTRIAL CHEMICALS

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PREFACE

This book is the outgrowth of a recognized need for the compilation in a single volume of important technical and economic data concerning the major industrial chemicals. We have found over a period of years in industry and teaching that information of this type cannot be obtained easily, not because it is unavailable, but because it is spread so widely and often hidden obscurely in a multitude of books, magazines, and pamphlets.

We have selected arbitrarily a group of 106 industrial chemicals, and [illegible]ed each one in accordance with the following outline:

1. Name and chemical formula.
2. Manufacturing processes in current use, including simplified flowsheets and important process variables.
3. Equations for the principal reactions involved; average yield expectation in per cent of theoretical.
4. Raw material requirements per unit weight of commercial product. In some cases, utility and labor requirements are shown.
5. Production chart for past 20 years.
6. Generalized use pattern.
7. Price chart for past 20 years.
8. Miscellaneous data, including physical properties, commercial grades, shipping regulations, and usual containers.
9. Economic aspects, generally including historical data, a discussion of competitive processes and products, recent trends in manufacturing and sales, actual and economic plant size, and approximate plant cost (as of 1946).
10. A map showing the location of manufacturing facilities in the United States.

We believe that information of this type will be of value, not only to those engaged in the manufacture and sale of chemicals and allied products, but also to those who use industrial chemicals or who have financial or other interests in concerns manufacturing or using industrial chemicals. The book should be a valuable asset to teachers [illegible] udents of science, engineering, and economics, and should be suita[illegible] se as a textbook in college courses in chemical technology and [illegible]cal economics.

The selection of the 106 chemicals has been limited to those made at part by synthetic or biochemical methods. Accordingly, none of variety of chemicals produced entirely by refining of natural pro is included. Practically all synthetic chemicals of major commercial importance have been selected, however, and a few minor ones, which, in our opinion, are destined for greater importance in the future.

The data and other information presented have been accumulated from so wide a variety of sources that a list of references would increase the size of the book markedly and also distort the appearance of the text. Government publications, technical and business periodicals, and advertising literature have served as the major sources of information. Private communications from many individuals in industry and business have confirmed much of the data. We have made every effort to keep the data as factual as possible and our calculations and estimates reasonably accurate. It would, of course, be a near miracle to have a compilation of this type free of errors. Accordingly we would greatly appreciate it if the reader would inform us of misstatements of fact or errors in estimates.

The authors gratefully acknowledge the assistance and suggestions made by members of the research department of Heyden Chemical Corporation and the chemical division of Corn Products Refining Company.

We wish to record with gratitude the encouragement and financial assistance which we received from the late Bernard R. Armour, who, at his untimely death on December 1, 1949, was president of the Heyden Chemical Corporation and chairman of the board of directors of the American Potash & Chemical Corporation. His help made this book possible.

We are also very grateful to Miss Thelma Sticka, who typed the manuscript under trying circumstances. We wish to acknowledge the help, advice, criticism, and encouragement of a great many other people, whose names we would list if space permitted.

W. L. FAITH
DONALD B. KEYES
RONALD L. CLARK

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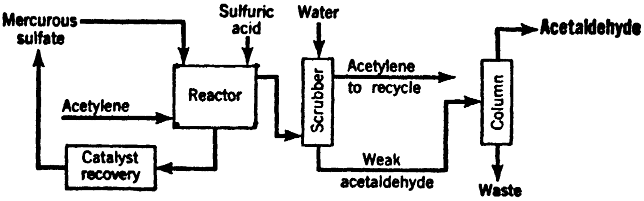
ACETALDEHYDE

CH_3CHO

From Acetylene



Reaction

$$CH{\equiv}CH + H_2O \xrightarrow{Hg_2SO_4,\ H_2SO_4} CH_3CHO$$

95% yield

Material Requirements

Basis—1 ton acetaldehyde

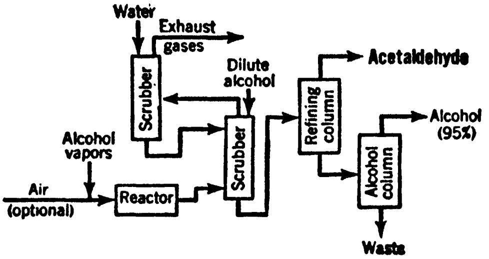
Acetylene	1,240 lb
Catalysts (sulfuric acid and mercurous sulfate)	Small

Process

Acetylene of high purity (99.5 per cent) is passed under a pressure of 15 psi into a reactor containing mercurous sulfate dissolved in 18 to 25 per cent sulfuric acid solution. The heat of reaction maintains the contents of the reactor at 70 to 100°C. During the reaction the mercurous sulfate is reduced to metallic mercury which settles to the bottom of the reactor as a sludge. A portion of the sludge is withdrawn every 15 min, and make-up catalyst is added intermittently at a rate that insures a complete change of catalyst every 8 hr. The sludge is sent to a catalyst-recovery system for reconversion to mercurous sulfate. Vapors of acetaldehyde, water, and unreacted acetylene are led from the reactor to a series of scrubbing towers and passed countercurrent to water to dissolve the acetaldehyde. A weak acetaldehyde solution leaves the bottom of the scrubber, and stripped acetylene gas leaves the top. The acetaldehyde solution is pumped to a column for concentration. Vapors leaving the top of the column may vary from 80 to 99 per cent acetaldehyde, depending on column efficiency. Crotonaldehyde is a by-product of the distillation. Scrubbed acetylene is recycled to the reactor.

Acetaldehyde is also obtained as a by-product in the manufacture of acetic anhydride from ethylidene diacetate prepared from acetylene. See *Acetic Anhydride.*

From Alcohol by Vapor-Phase Oxidation or Dehydrogenation



Reaction

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2 \quad \text{or}$$

$$CH_3CH_2OH + \tfrac{1}{2}O_2 \rightarrow CH_3CHO + H_2O$$

85–95% yield

Material Requirements (Major)

Basis—1 ton acetaldehyde

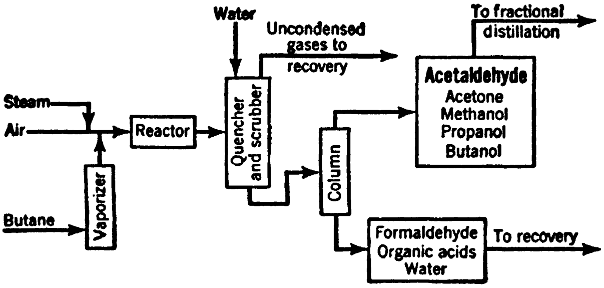
Alcohol (100%)	2,300 lb

Process

Alcohol vapors (50 to 95 per cent) and preheated air are mixed in such proportions that the exothermic heat of oxidation will just exceed the absorbed heat of dehydrogenation, in which case the reaction will proceed without the external application of heat. The vapors pass through a reactor containing a silver gauze catalyst. Reactor temperature depends on the air–ethanol–steam ratio and the velocity of the gases over the catalyst and may vary from 375 to 550°C. Exit gases from the converter, containing alcohol and acetaldehyde, are led to a scrubbing column where cold dilute alcohol cools the gases and dissolves both the alcohol and acetaldehyde. The stripped gases leaving the top of the scrubber are scrubbed again with water and released to the atmosphere. The dilute alcohol–acetaldehyde solution from the bottom of the scrubbing column is rectified in a refining column to produce 99 per cent acetaldehyde as overhead. The dilute alcohol solution leaving the bottom of the column is concentrated in the conventional manner. Conversion per pass generally ranges from 25 to 35 per cent.

When a straight dehydrogenation process, the usual procedure, is being carried out, a chromium-activated copper catalyst may be used. The temperature of the reaction is maintained by external heating at 260 to 290°C. The rest of the process is essentially the same as that described previously except that the exhaust gas from the scrubber is chiefly hydrogen, which may be recovered for use. Conversion of alcohol per pass ranges from 30 to 50 per cent.

From Butane



Reaction

$$C_4H_{10} + O_2\ (\text{air}) \xrightarrow{\text{Steam}} \begin{array}{c} CH_3CHO \\ HCHO \\ CH_3COCH_3 \\ 64\%\ \text{yield} \end{array} + \begin{bmatrix} \text{Methanol} \\ \text{Propanol} \\ \text{Butanol} \\ \text{Organic acids} \end{bmatrix} + \begin{bmatrix} CO_2 \\ CO \\ N_2 \end{bmatrix}$$

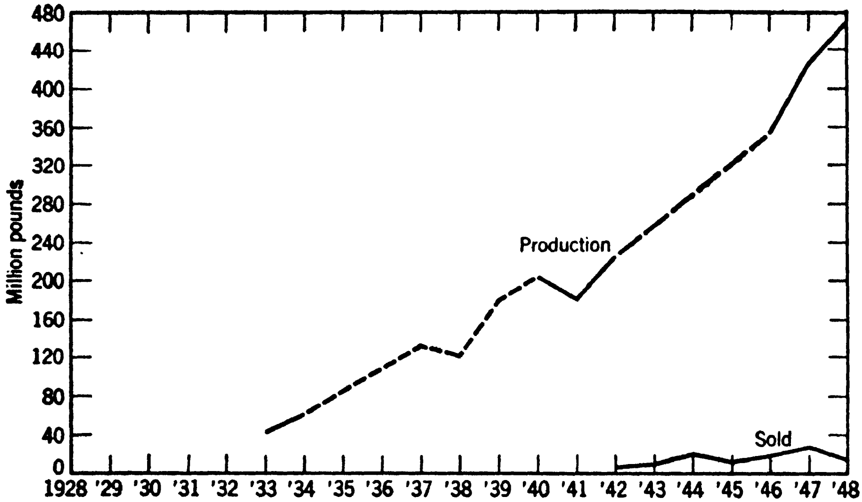
Material Requirements

Basis—1 ton acetaldehyde

Butane	8,700 lb
Steam	189,000 lb
Air	43,500 lb

Process

Liquid butane (1 part by volume) is heated to 300°F and passed to a mixing chamber maintained at 550°F with an admixture of air (10 parts by volume) and steam (70 parts by volume) preheated to 750°F. This mixture is caused to travel at high velocity through the chamber, where it is mixed at high turbulence and the butane is immediately raised to the reaction temperature. The gases pass through the reactor (50 to 200 psi) in 0.3 sec, are quenched by water to 300°F, and scrubbed. The uncondensed gases leave through a pressure-release valve to be recovered and recycled. The mixture of condensed oxygenated compounds and water is distilled. The bottoms consist of formaldehyde, organic acids, and water, while the overhead contains acetaldehyde, acetone, methanol, propanol, and butanol, which may be separated by repeated fractional distillation. Butane, so processed, yields 23 per cent by weight acetaldehyde plus 15 per cent formaldehyde, 10 per cent acetone, 7 per cent organic acids, and 3 per cent each of methanol, propanol, and butanol.



Production—Acetaldehyde

Use Pattern

	1947 (est.), per cent
Acetic acid and anhydride	75
Butanol	20
Miscellaneous	5
	100

Miscellaneous

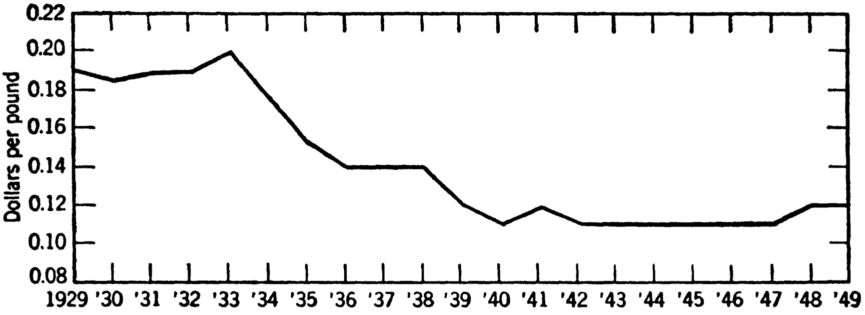
Properties. Colorless, fuming, flammable liquid with a pungent, fruity odor.

Mol. wt.	44.05	M.P.	−123.5°C
Sp. gr.	0.7801 20°C/20	B.P.	20.9°C

Weight per gallon 6.49 lb (20°C)

Soluble in all proportions with water, alcohol, ether, and benzene at room temperature.

Flash point (open cup)	−40°F
Ignition temperature	365°F
Vapor density (air = 1)	1.52
Explosive limits (% by volume in air)	Lower 4 Upper 57



Price—Acetaldehyde

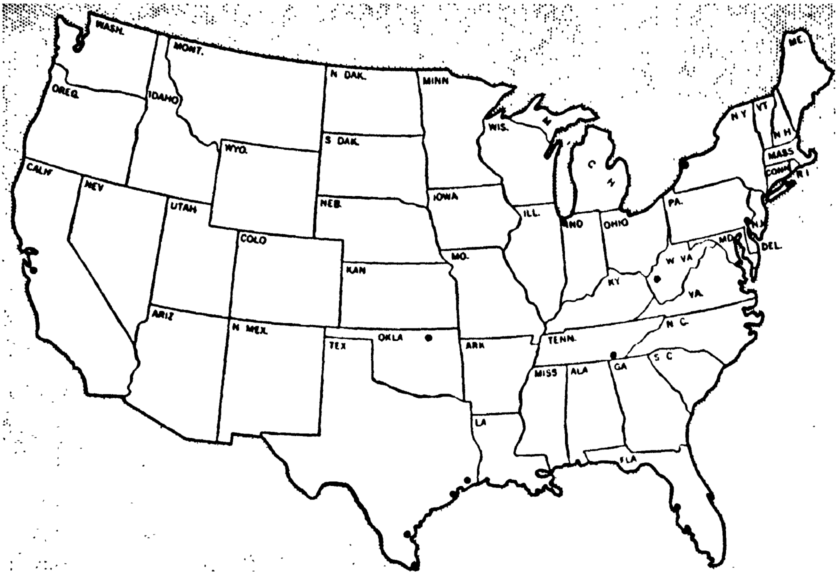
Grades. Technical (containing 99 per cent minimum acetaldehyde).

Containers and Regulations. Tank cars, steel drums, cylinders, tins, and bottles. Acetaldehyde is classed as a flammable liquid and requires a red ICC shipping label. ·

Economic Aspects

For strictly aldehyde uses, acetaldehyde is overshadowed by the simpler member of the aldehyde series, formaldehyde. Consequently, it is used primarily for the manufacture of special chemicals, for example, acetic acid, acetic anhydride, pentaertythritol, and butanol. Its natural manufacturers, therefore, are the producers of such chemicals or those manufacturing other chemicals from acetylene or ethylene. Over 95 per cent of the acetaldehyde made is used in the same plant in which it is produced. It is also produced as a by-product or at best a joint product with other chemicals in the oxidation of hydrocarbons (see *Formaldehyde*), the manufacture of acetic anhydride from ethylidene diacetate, and the conversion of alcohol to butadiene. Accordingly, interprocess competition is related to many factors which must be evaluated for the particular conditions extant at a given plant. Major production, however, is from alcohol which, in turn, is largely derived from ethylene. Just what will be the impact of the war-developed Wulff process which produces two raw materials, acetylene and ethylene, from which acetaldehyde is made, remains to be seen.

There are only a few manufacturers of acetaldehyde, and so figures on economic plant size and cost are not readily available. In the acetylene hydration process, the determination of the smallest economic unit is based on the economic sizes of the carbide furnace and refining still, rather than of the intermediate units. The economic size of a carbide furnace is generally considered to be a 2,500-ton-per-year unit. Such a furnace could furnish sufficient raw material for 1,500,000 lb acetaldehyde annually if all the acetylene were so used. A 50,000,000-lb-per-yr acetaldehyde plant costs about $825,000.

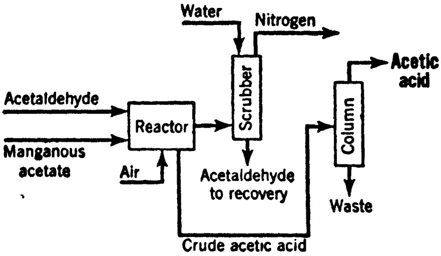


Location of Acetaldehyde Plants

ACETIC ACID

CH_3COOH

From Acetaldehyde



Reaction

$$CH_3CHO + \tfrac{1}{2}O_2 \xrightarrow{(CH_3COO)_2Mn} CH_3COOH$$

88–95% yield

Material Requirements

Basis—1 ton acetic acid (100%)

Acetaldehyde	2,200 lb
Manganous acetate	6.6 lb
Air	8,040 cu ft

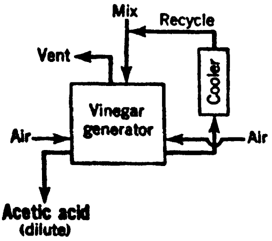
Process

A highly concentrated acetaldehyde solution (99 to 99.8 per cent) is introduced into a stainless-steel reaction kettle in which air at 70 to 75 psi bubbles through the liquid (55 to 65°C) which contains 0.1 to 0.5 per cent manganous acetate used to decompose the explosive intermediate: peracetic acid. Batchwise, 9,000 lb acetaldehyde can be completely oxidized in 12 hr. The gases leaving the reactor are scrubbed with water, releasing nitrogen to the atmosphere. The dilute acetaldehyde solution leaving the bottom of the scrubber is sent to a column for recovery. The crude acetic acid (94 to 96 per cent) is discharged from the reactor and continuously rectified to yield 99 per cent glacial acetic acid.

In some modern plants the oxidation is carried out continuously rather than batchwise. The catalyst in this case is cobalt acetate dissolved in acetic acid. The reactor is operated at 15 psi and 70 to 80°C. Approximately 4 moles of air enter the converter per mole of acetaldehyde.

An alternative vapor-phase oxidation process currently in use makes use of a mixture of alcohol and acetaldehyde, which on catalytic air oxidation yields both acetaldehyde and acetic acid as products. By recycling the acetaldehyde, adding only alcohol to the system as make-up, and removing only acetic acid, the process becomes essentially a catalytic vapor-phase alcohol oxidation to acetic acid. Equipment used is similar to that described under *Acetaldehyde.*

From Alcohol by Quick-Vinegar Fermentation



Reaction

$$C_2H_5OH + O_2 \text{ (air)} \rightarrow CH_3COOH + H_2O$$

80–90% yield

Material Requirements

Basis—1 ton acetic acid (100%)

Alcohol (95%)	1,950 lb
Nutrient	Small
Air	11,000 lb

Process

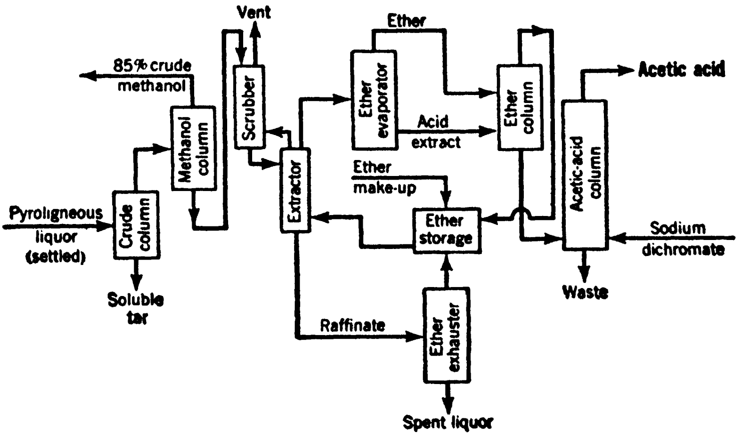
A mix consisting of equal parts of dilute alcohol (S.D.—18) and vinegar (10 per cent), and a nutrient is introduced through a sparger at the top of a large closed tank (1,000- to 15,000-gal capacity) packed with beechwood shavings. The mix contains about 10.5 per cent alcohol and 1 per cent acetic acid. The sparger evenly distributes the mix over the top of the bacteria-laden (*Bacterium aceti*) shavings whence it trickles to the bottom of the tank to complete one cycle of circulation. Air, regulated by a butterfly valve in the vent, enters near the bottom and passes up through the shavings countercurrent to the trickling mix. Heat, generated by the oxidation process, is responsible for the air movement but must be controlled by cooling the bottom liquor before recycling to maintain the proper temperature (30 to 35°C) for bacterial activity. The recycling of liquor is continued until the mix has reached the optimum acidity (10 to 10.5 per cent acetic acid) and is then discharged. A new mix is immediately introduced to continue the recycling process. This process can produce only dilute acetic acid since the bacteria cease to survive at 12 to 14 per cent acidity. A 2,500-gal batch of 10.5 per cent acetic acid can be processed in 8 to 10 days.

From Wood Distillation

Pyroligneous acid liquor is one of the products obtained by the destructive distillation of hardwood. The wood is charred in either continuous or batchwise retorts in the absence of air. Processes vary in procedure in such details as size and type of wood used and length of predrying periods (2 days to 18 months), but all produce about the same quality and quantity of charcoal and raw pyroligneous liquor. One cord (4,000 lb) of hardwood yields about 250 gal (2,260 lb) of pyroligneous acid liquor (containing 7 per cent acetic acid or equivalent, 4 per cent crude methanol and acetone, 9 per cent tar and oils, and 80 per cent water), 1,000 lb of charcoal, and 7,500 cu ft of fuel gas (53 per cent carbon dioxide, 27 per cent carbon monoxide, and 15 per cent methane) having an average heating value of 250 to 300 Btu per cu ft.

The charcoal is cooled, graded, and packaged. The vapors are condensed, and the noncondensable gases are used for fuel. The resulting liquor is allowed to settle to remove insoluble tar, and the clear decanted liquor containing 6 to 7 per cent acetic acid is utilized as the starting material in the following processes.

From Pyroligneous Liquor (Coahran Cold-Solvent Extraction Process)



Recovery

98–99%

Material Requirements

Basis—1 ton acetic acid (100%) and
150 gal crude methanol (100%)

Pyroligneous liquor	4,170 gal	Sodium dichromate	2–4 lb
Solvent ether loss	25 lb	Water	100,000 gal
Steam	15,680 lb		

Process

Settled pyroligneous acid is charged to a "crude" column in which acetic acid and methanol are vaporized, leaving soluble tar behind. These mixed vapors may be partially condensed by furnishing heat to the ether evaporator before the vapors enter the methanol column from which 85 per cent methanol vapors are removed as overhead. Dealcoholized liquor leaves the bottom of the column, passes through a cooler, and is led to the liquid extraction column in which acid is extracted by cold ethyl ether, 2.6 volumes of ether being used per volume of liquor.

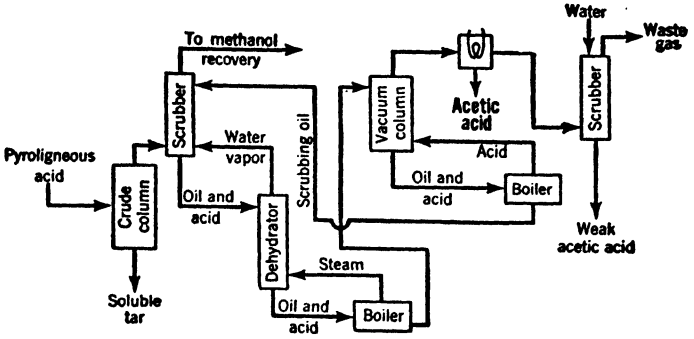
The raffinate, or water layer, is discharged from the bottom of the extractor to the ether exhauster in which dissolved ether is stripped from solution and returned to storage. The spent waste liquor leaving the bottom of the column usually contains less than 0.1 per cent acetic acid.

The extract, or ether layer, containing 2 to 3 per cent acetic acid is led to the ether evaporator and ether column in which the ether and acid are separated by distillation. The ether is removed as overhead from the column, condensed, and returned to ether storage. Crude acetic acid (70 per cent), containing some wood oils and tar, is discharged from the bottom of the column still.

The 70 per cent crude acetic acid is treated with sodium dichromate and rectified in a batch still in which volatile impurities and water distil off as constant-boiling mixtures, followed by 99 per cent acetic acid.

By slight variations in plant design and operation, ethyl acetate may be used as an extraction agent in place of ether.

From Pyroligneous Liquor (Suida Process)



Recovery

95-96%

Material Requirements

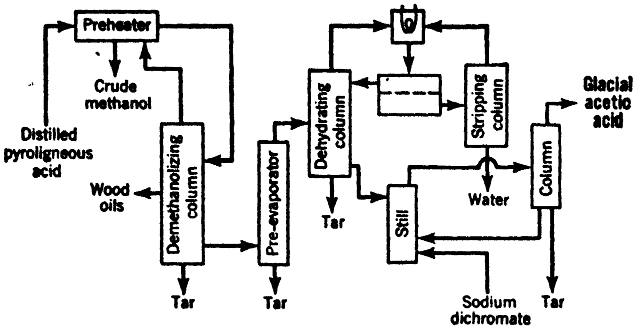
Basis—1 ton acetic acid (100%)

Pyroligneous liquor	17 tons	Water (including retorts)	240,000 gal
Scrubbing oil	500–600 lb	Steam	32–37 tons

Process

Settled pyroligneous acid is distilled to remove soluble tar. Vapors containing methanol and acetic acid pass to a countercurrent scrubbing column in which a wood-oil fraction dissolves the acid, allowing dilute methanol vapors (4 per cent) to pass overhead to a methanol-recovery system. The wood-oil–acid solution passes through a dehydrating column, where water is removed, to a vacuum column in which the acetic acid is separated from the oil. The oil is returned to a storage tank for further use, and the acetic-acid vapors are rectified in a vacuum column. Concentrated acetic acid (92 per cent) is removed from a partial condenser. The exit vapors from the condenser are scrubbed with water to produce weak acid (15 per cent). Alternatively, 92 per cent acid may be withdrawn as a liquid from the column plate on which it concentrates, and the 15 per cent weak acid may be taken off as overhead.

From Pyroligneous Acid (Othmer Process)



Recovery

97–98%

Material Requirements

Basis—1 ton acetic acid (100%) and
187 gal crude methanol (100%)

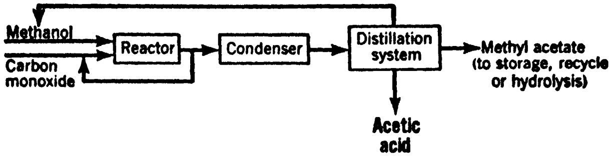
Pyroligneous acid	4,240 gal	Sodium dichromate	34 lb
Withdrawing agent	2.5 lb	Steam	55,200 lb

Process

Distilled pyroligneous acid is pumped to a demethanolizing column where crude methanol is removed overhead, wood oil is removed from one of the middle plates, and a crude acetic-acid fraction is withdrawn from one of the lower plates. Some tar is removed from the bottom of the column. The crude acetic acid is led to a pre-evaporator and a dehydrating column where water is removed overhead by means of a withdrawing agent, such as butyl acetate or ethylene dichloride. The withdrawing agent forms a low-boiling azeotrope with the water. These vapors are condensed and sent to a separator where the top layer, the withdrawing agent, is returned to the dehydrating column, and the lower water layer is led to a stripping column from which the water, containing less than 0.01 per cent acetic acid, is removed as bottoms. Vapors leaving the top of the stripping column are condensed and returned to the separator.

The dehydrated acetic acid is removed from near the bottom of the dehydrating column and sent to a still and rectifying column for treatment with sodium dichromate and a final distillation to yield glacial acetic acid as overhead.

From Methanol and Carbon Monoxide



Reaction

$$CH_3OH + CO \rightarrow CH_3COOH$$

90% Yield

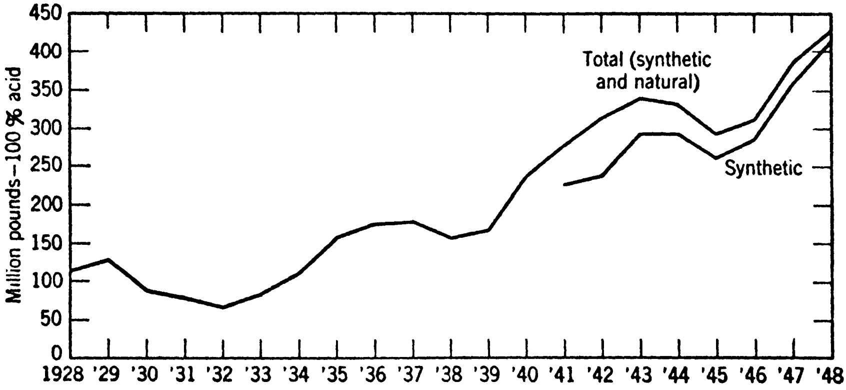
Material Requirements

Basis—1 ton acetic acid
(including contained acid in methyl acetate)

Methanol	1,200 lb
Carbon monoxide	1,050 lb

Process

A gas mixture consisting of 90 to 95 per cent carbon monoxide, 0 to 5 per cent hydrogen, and 5 per cent methanol is passed through a reactor containing an activated carbon catalyst. The catalyst may be promoted with not more than 10 per cent titania, alumina, or silica. The reaction is carried out at about 700 atm and 350°C.



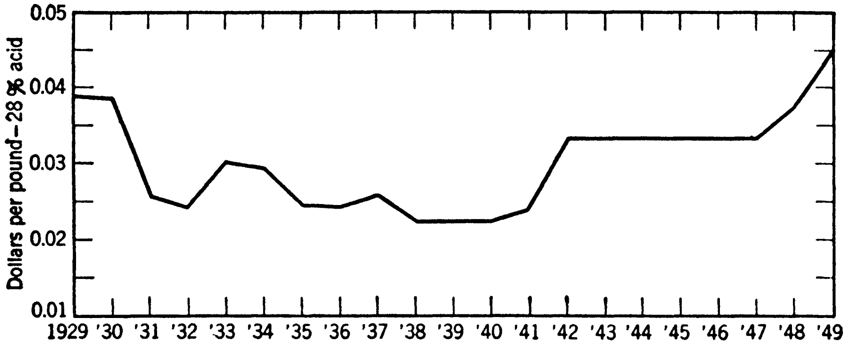
Production—Acetic Acid

Exit gases from the reactor are cooled to yield condensate consisting of acetic acid, methyl acetate, and unconverted methanol. The amount of methyl acetate present depends on the temperature at which the reaction is conducted. Below 300°C very little acetate is formed, but the rate of reaction is comparatively slow. Above 300°C both reaction rate and percentage of methyl acetate increase; 350°C appears to be the optimum temperature.

Condensate from the cooler is fed to a series of fractionating columns to separate unconverted methanol, methyl acetate, acetic acid, and water. The methyl acetate may be used as such or hydrolyzed to recover methanol and acetic acid. It may also be recycled along with fresh methanol.

Use Pattern*

	1947 (est.), per cent
Acetic anhydride	60
Solvents (acetates)	30
Miscellaneous	10
	100



Price—Acetic Acid

Miscellaneous

Properties. (Glacial acetic acid.) Colorless liquid with a pungent, characteristic odor and a sharp acid taste.

Mol. wt.	60.05	M.P.	16.6°C
Sp. gr.	1.049 20°/4°	B.P.	118.1°C
	Weight per gallon	8.64 lb (20°C)	

Soluble in all proportions with water, alcohol, glycerin, and ether at room temperature. Insoluble in carbon disulfide.

Flash point (closed cup)	104°F
Ignition temperature	800°F
Vapor density (air = 1)	2.07
Explosive limits (% by volume in air)	Lower 4

---

* For synthetic acid only.

Dangerous fire hazard in contact with chromic acid, sodium peroxide, or nitric acid.

Grades. USP: glacial (99.4 per cent) and dilute (36 to 37 per cent). Commercial: dilute (6, 28, 30, 36, 56, 60, 70, and 80 per cent), pure (C.P.), and technical (80 per cent).

Containers and Regulations. Tank cars, tight barrels, aluminum drums, carboys, and bottles. Glacial acetic acid expands on solidification and may burst the container unless stored at a temperature above 16°C (60.8°F). It requires a white ICC shipping label.

Economic Aspects

Interprocess competition in acetic-acid manufacture is threefold: synthetic versus by-product, various synthetic processes versus each other, and various by-product recovery processes in the wood-distillation industry versus each other. Synthetic processes, particularly the oxidation of acetaldehyde, have been the cause of cheap acetic acid, but, as long as there is a market for charcoal and other by-products of the wood-distillation industry, some acid will be made by this means. In 1947 approximately 7 per cent of acetic-acid production was by the wood-distillation industry compared with 87 per cent in 1927 and 28 per cent in 1937. These figures are based only on new production of concentrated acid; both recovered acid and vinegar are omitted. In 1948 recovered acid, chiefly from acetylation processes, amounted to more than four times new acid production. Vinegar production in recent years has varied from 50,000,000 to 70,000,000 lb annually (calculated as 100 per cent acid).

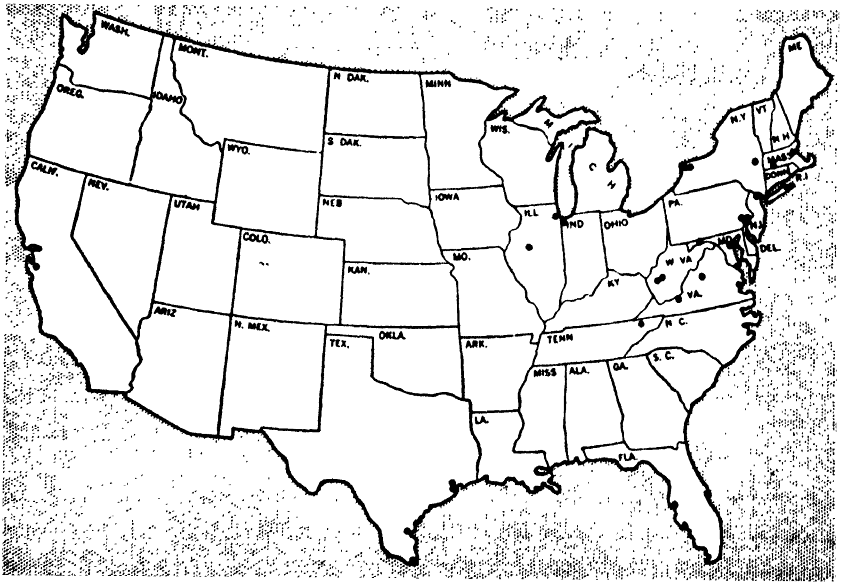
In the synthetic field, competition is centered around intermediate raw-material manufacture, chiefly acetylene. A great deal of development work has been done on hydrocarbon cracking processes by means of which acetylene and ethylene may be produced from natural gas or natural gasoline. Since acetaldehyde may be produced from either acetylene or ethylene, these processes may be a factor in future acetic-acid manufacture. The possible impact of the Fischer–Tropsch process (see *Ethyl Alcohol*) on acetic-acid production has not yet been determined but may be of considerable importance.

One new plant produces acetic acid along with various other organic compounds by the oxidation of butane (see *Formaldehyde* and *Acetaldehyde*). Acetic acid is also produced as a by-product in various organic manufacturing processes (see *Furfural*).

Competition among various processes for recovery of acetic acid from pyroligneous liquor centers around steam costs. The liquid–liquid extraction process is the most widely used of the three processes described.

Very little acid is now made by the classical method of treatment of "gray acetate of lime" with sulfuric acid. The quick-vinegar process is limited to the production of dilute acid for the food industry and the manufacture of low-molecular-weight esters, such as ethyl acetate. Very small vinegar plants can be built, although during World War I one plant had a capacity of over 10,000 tons annually. A plant of such size is no longer considered economical. A typical modern quick-vinegar generator is approximately 10 ft in diameter and 20 ft high, with a daily production capacity of 80 to 100 gal distilled vinegar.

Plant costs for the various processes depend, of course, on the size of the plant. A by-product wood-distillation plant processing less than 60 cords of wood per day (7,150 lb acetic acid) can hardly be considered competitive. Such a plant, complete with acetic-acid- and methanol-recovery units, would probably cost $9,000 per daily cord capacity. In the synthetic process the smallest economic plant would produce 1,000 tons of acetic acid per year, which corresponds roughly to the amount of carbide produced from a furnace of usual size. Few plants, however, produce less than 15,000 tons annually, and one plant produces over 50,000 tons. An acetaldehyde oxidation plant of 25,000 tons annual capacity costs about $30 per annual ton of acetic acid.



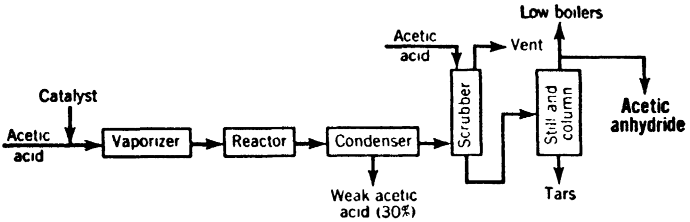
Location of Synthetic-Acetic-Acid Plants

(70 per cent), glacial acetic acid, and mercuric oxide. The proportions that may be used consist of 0.5 per cent mercuric oxide and enough oleum in acetic acid to give 1.5 per cent excess sulfuric acid. The catalyst is usually present in the reactor to the extent of 2.5 per cent mercuric oxide. The reaction is maintained at 60 to 85°C for a sufficient length of time to convert the acid to ethylidene diacetate. The contents of the reactor are then dumped to a sludge settler whence the settled solids are led to a furnace in which organic material is burned off and the mercuric oxide is removed to be re-used in the catalyst preparation. One pound of contained mercury in the catalyst yields 100 lb ethylidene diacetate.

The clarified liquor from the sludge settler is treated with calcium or sodium acetate, to neutralize the sulfuric acid present, and led to a vacuum column. The ethylidene diacetate is taken off as overhead. The system may be modified, and often is, to produce both vinyl acetate ($C_2H_2 + CH_3COOH \rightarrow CH_3COOCH{=}CH_2$) and ethylidene diacetate, by removing the former from the reactor as a vapor, separating it from the accompanying acetic acid and ethylidene diacetate, and refining.

Ethylidene diacetate is converted to acetic anhydride and acetaldehyde by distillation in the presence of 1 to 3 per cent sodium pyrophosphate or zinc chloride. Phosphoric acid may also be added to reduce tar formation. Conversion of ethylidene diacetate per cycle approaches 75 per cent. The recovered ethylidene diacetate (B.P. 166°C) is recycled.

From Acetic Acid (Ketene)



Reaction

$$CH_3COOH \rightarrow CH_2{=}C{=}O + H_2O$$

$$CH_3COOH + CH_2{=}C{=}O \rightarrow (CH_3CO)_2O$$

85–89% yield

Material Requirements

Basis—1 ton acetic anhydride

Acetic acid	2,700 lb
Catalyst	Small

Process

Vapors of glacial acetic acid containing 1 to 4 ppm triethylphosphate or phosphoric acid (1 to 3 ppm pyridine or ammonia may also be added to the vapors) are passed through an empty carbon tube heated to 750 to 850°C and held under reduced pressure (35 mm).

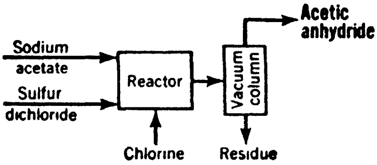
The reactor exit vapors containing acetic anhydride, acetic acid, ketene, and water are led to a series of condensers where weak acetic acid (30 per cent) is condensed before it can react with the ketene. The uncondensed ketene is absorbed in acetic acid to give acetic anhydride (90 per cent purity), which is then fractionated to yield a specification product.

Ketene may also be prepared from acetone according to the equation:

$$CH_3COCH_3 \rightarrow CH_2{=}C{=}O + CH_4$$

Acetone vapors are passed through a void chrome–iron tube. The temperature of the tube is 650 to 670°C, and the contact time is about 0.25 to 5 sec. The unchanged acetone is condensed and recycled. The gaseous ketene is absorbed in glacial acetic acid to give acetic anhydride. Yields based on acetone are about 80 to 95 per cent.

From Sodium Acetate



Reaction

$$8CH_3COONa + SCl_2 + 2Cl_2 \rightarrow 4(CH_3CO)_2O + 6NaCl + Na_2SO_4$$

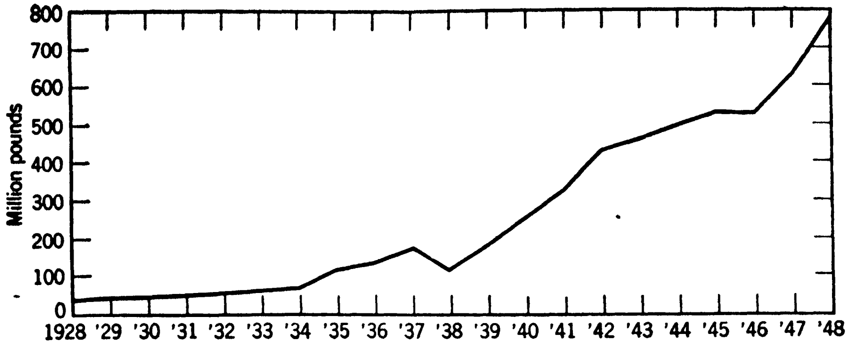
Material Requirements (Theoretical)

Basis—1 ton acetic anhydride

Sodium acetate	3,200 lb
Sulfur dichloride	505 lb
Chlorine	350 lb

Process

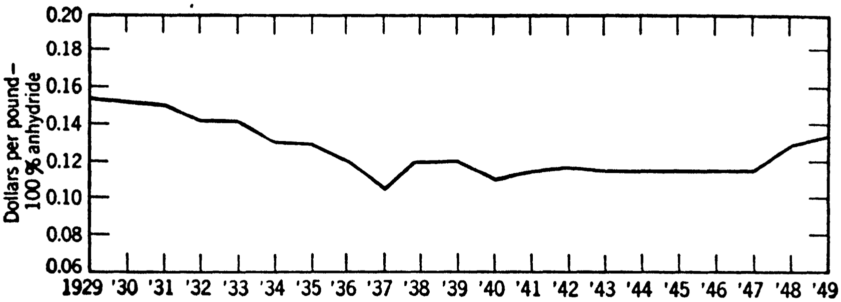
Sodium acetate and sulfur dichloride (6.3-to-1 weight ratio) are mixed in a reactor and then subjected to the action of chlorine. The reaction mass is maintained at 15 to 25°C by cooling coils. When the reaction is complete, the mass is heated for 2 hr at 80°C. The acetic anhydride may be either distilled directly from the reactor or separated from the solid salts formed and distilled separately under vacuum.



Production—Acetic Anhydride

Use Pattern

	1947 (est.), per cent
Rayon	75
Resins and plastics	20
Other (aspirin, perfumes, flavor bases, textile processes)	5
	100



Price—Acetic Anhydride

Miscellaneous

Properties. Colorless, highly refractive liquid with a strong acetic odor.

Mol. wt.	102.09	M.P.	−73.1°C
Sp. gr.	1.083 20°C/20	B.P.	139.9°C

Weight per gallon 9.01 lb (20°C)

Soluble in all proportions with alcohol and ether at room temperature. In cold water, it is soluble to the extent of 13.6 g per 100 ml but decomposes in hot water.

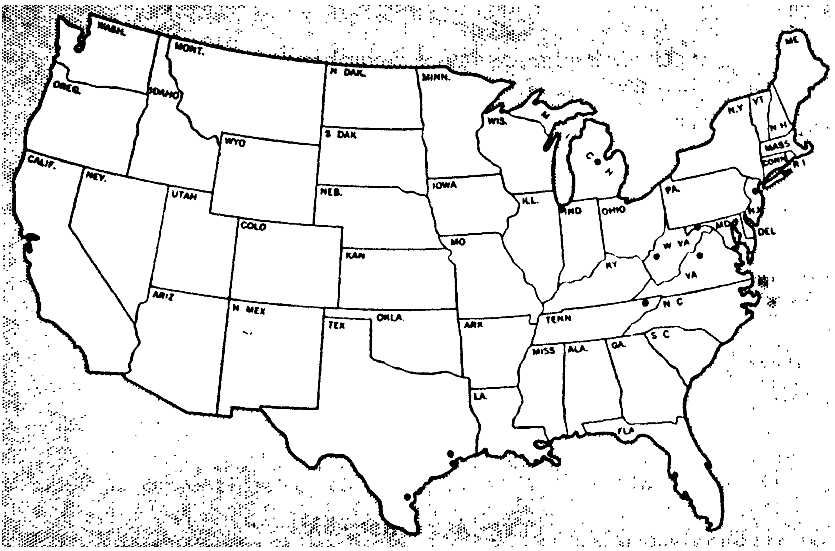
Flash point (open cup)	150°F
Ignition temperature	752°F
Vapor density (air = 1)	3.52
Explosive limits (% by volume in air)	Lower 2.67
	Upper 10.13

Grades. Technical (75, 85, 90 to 95 per cent), C.P.

Containers and Regulations. Aluminum drums and tank cars, carboys, and glass bottles. A white ICC shipping label is required.

Economic Aspects

Acetic anhydride is made in greatest quantity by its chief users, cellulose acetate manufacturers, or by well-integrated organic-chemical manufacturers, who make a wide variety of related compounds. Of the various processes described in this section, all may be considered competitive except the sodium acetate and sulfur dichloride process which has nearly disappeared. At one time, considerable volume was made from sodium acetate and acetyl chloride, but this process is now obsolete.



Location of Acetic Anhydride Plants

Most plants vary in size from 2,500,000 to 20,000,000 lb per yr. It has been estimated that a 6,000,000-lb-per-yr plant using sulfur dichloride and sodium acetate as starting materials would cost $600,000, whereas one of similar capacity using the catalytic dehydration of acetic acid could be built for $375,000. Construction costs of current process plants are probably in the same range as the latter.

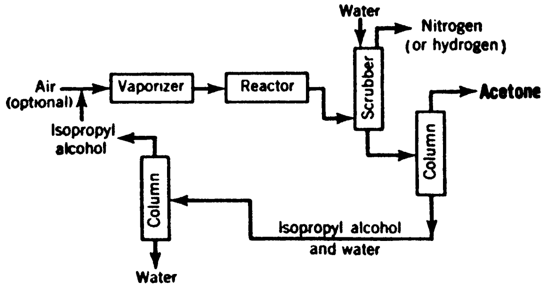
Another factor that must be considered in the choice of process for manufacturing acetic anhydride is the hazard involved in plant operation. Ketene, for example, is very poisonous, and the ethylidene diacetate process involves an explosion hazard.

It is reasonable to believe that the future of acetic anhydride manufacture will be closely related to the future of cellulose acetate and hence will be governed by gains or losses of the latter in the rayon and plastics field.

ACETONE

CH_3COCH_3

From Isopropyl Alcohol



Reaction

$$(CH_3)_2CHOH + \tfrac{1}{2}O_2 \text{ (air)} \rightarrow CH_3COCH_3 + H_2O \quad \text{or}$$

$$(CH_3)_2CHOH \rightarrow CH_3COCH_3 + H_2$$

85% yield

Material Requirements (Major)

Basis—1 ton acetone

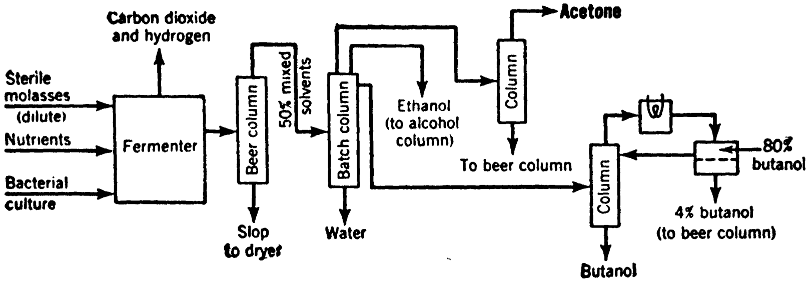
Isopropyl alcohol	2,435 lb

Process

Air saturated with isopropyl alcohol vapors is passed through a reactor containing a catalytic bed of silver or copper maintained at a temperature of 400 to 600°C. The hot gases are partially cooled and scrubbed with water; nitrogen is released to the atmosphere. The water solution of acetone and unconverted isopropyl alcohol is passed to a rectifying column where concentrated acetone is taken off as the overhead and the alcohol and water as the bottoms. To recover isopropyl alcohol, the bottoms are led to a column where a binary constant-boiling mixture containing 91 per cent isopropyl alcohol is taken off the top and water is discharged at the bottom. The 91 per cent isopropyl alcohol may be recycled without further purification.

In the straight dehydrogenation process, isopropyl alcohol is dehydrogenated by passing the preheated vapors over a brass or copper catalyst at 500°C and 40 to 50 psi. The effluent gases are condensed and scrubbed with water as in the afore-mentioned process. However, the condenser and scrubber may be maintained at 40 to 50 psi in order to increase their efficiency. At this pressure the scrubber requires 50 per cent fewer theoretical plates and about 0.2 lb water per lb acetone (in contrast to 0.7 lb water per lb of acetone at atmospheric pressure) to release hydrogen which is materially free from entrained acetone. The yield of acetone is about the same as that produced by the oxidation–dehydrogenation process.

From Carbohydrates by Fermentation



Reaction

$$(C_6H_{10}O_5)_x \xrightarrow{H_2O} C_6H_{12}O_6 \rightarrow$$
Starch Glucose

$$CH_3COCH_3 + CH_3CH_2CH_2CH_2OH + C_2H_5OH + CO_2 + H_2$$

Yields

$$\text{1 gal molasses (6–6.6 lb sugar)} = \left\{ \begin{array}{l} \text{1.45–1.65 lb butanol} \\ \text{0.4–0.65 lb acetone} \\ \text{0.07–0.1 lb ethyl alcohol} \\ \text{plus } CO_2 \text{ and } H_2 \end{array} \right.$$

$$\text{1 bu corn (33 lb starch)} = \left\{ \begin{array}{l} \text{6–8 lb butanol} \\ \text{3–4 lb acetone} \\ \text{1–}1\tfrac{1}{2}\text{ lb ethyl alcohol} \\ \text{15–16 lb—60\% } CO_2\text{, 40\% } H_2 \end{array} \right.$$

Material Requirements

Basis—1 ton acetone

Molasses	3,340 gal
Water	44,560 lb
Nutrients	17 lb

Process

Molasses is diluted with water to a concentration of approximately 5 per cent sugar, sterilized, cooled to 85°F, and pumped to a fermenter. A culture of bacteria (*Clostridium saccharobutyl acetonicum liquefaciens*) grown in sterile molasses is added to start the fermentation. Protein nutrients and an alkaline buffer to control the *p*H are also added to improve yields.

After fermentation has proceeded for 36 to 48 hr, the beer (fermentation mixture) containing 1.5 to 2.5 per cent mixed solvents is pumped to a column whence a 50 per cent solvent mixture is taken off overhead and distillers' slop is removed as bottoms. This slop may be dried and sold as animal feed or utilized as a source of riboflavin and other components of the vitamin B complex, since it has been discovered that the bacteria used in the fermentation synthesize vitamins. Another by-product is a mixture of carbon dioxide and hydrogen which is evolved during the fermentation.

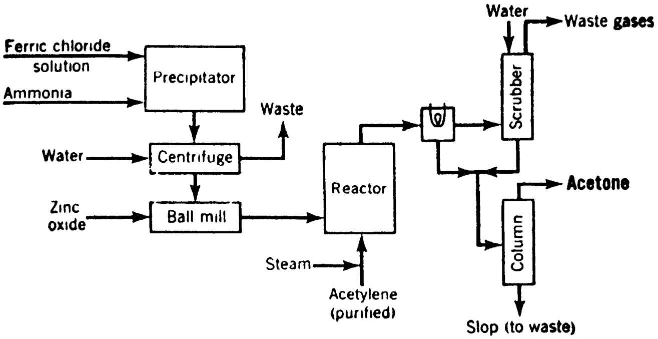
The mixed-solvent vapors from the beer column are led to a batch fractionating column from which three fractions (acetone, ethanol, and butanol) are removed overhead, leaving water as bottoms. The acetone and ethanol fractions are purified by conventional fractionation. The butanol fraction, containing about 15 per cent water, is led to a column from which vapors containing 70 per cent butanol and 30 per cent water are removed overhead. On condensation, two layers are formed. The top layer (80 per cent butanol and 20 per cent water) is returned to the butanol column, and the bottom layer (4 per cent butanol and 96 per cent water) is returned to the beer column.

The yield of mixed solvents is approximately 30 per cent by weight based on the sugar charged. Solvent yield ratios are 60 per cent butanol, 30 per cent acetone, and 10 per cent ethanol by weight.

Sterilized degermed cornstarch mash may be substituted for the molasses, in which case the fermentation is carried out at 98°F using bacteria of the *Clostridium* genus such as *Clostridium acetobutylicum.*

Considerable more care must be exercised in carrying out the butanol–acetone fermentation than either ethyl alcohol or acetic-acid fermentations. The latter are biologically stable fermentations which usually proceed readily and easily. Ethyl alcohol fermentation, of course, may produce low yields when conditions are unfavorable. On the other hand, the butanol–acetone fermentation is biologically unstable and may fail completely when contaminated. Numerous instances of contamination by bacteriophage have been encountered commercially, and on several occasions plants have had to suspend operation until the entire plant could be immunized. Accordingly, absolute cleanliness, experienced personnel familiar with "phage" symptoms, and the maintenance of a vigorous rapid fermentation are necessities in the butanol–acetone fermentation.

From Acetylene



Reactions

$$C_2H_2 + H_2O \rightarrow CH_3CHO$$

$$CH_3CHO + H_2O \rightarrow CH_3COOH + H_2$$

$$2CH_3COOH \rightarrow CH_3COCH_3 + CO_2 + H_2O$$

$$\text{Over-all} \quad 2C_2H_2 + 3H_2O \rightarrow CH_3COCH_3 + CO_2 + 2H_2$$

75–85% yield

Material Requirements

Basis—1 ton acetone

Acetylene	2,240 lb
Steam (for reaction)	19,000 lb
Catalyst	Figure not available

Process

Acetone is manufactured directly from steam and purified acetylene by passing a steam–acetylene mixture through a catalyst bed (Fe_2O_3–ZnO) at elevated temperatures and recovering acetone from the reaction gases.

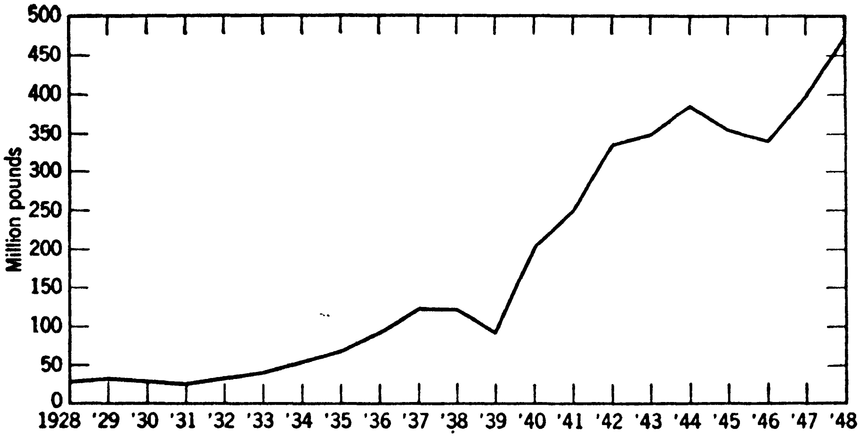
The catalyst is prepared by ammonia precipitation of ferric hydroxide from a 45 per cent ferric chloride solution. The hydrate is purified by centrifugation and washing, mixed with zinc oxide, ground in a ball mill, with 3/8-in. iron balls, and transferred (along with the iron balls) to a series of reactors.

Each reactor consists of a cylindrical group of vertical tubes, open at the bottom, which fit into a reactor head. The catalyst and iron balls are held in the tubes in conventional perforated baskets. The upper ends of the tubes lead to a manifold connected to a condenser. The reactors are so designed that they may be moved from place to place on a monorail. Each reactor tube, containing 270 lb of fresh catalyst, is conveyed to a dryer where the catalyst is dried *in situ* for 8 hr.

After the catalyst is dried, the reactor containing the dried catalyst is transported by monorail to a molten salt ($NaNO_3$–KNO_3) bath. Steam is passed through the catalyst bed for 2 hr to effect thorough hydration. After 2 hr, a mixture of steam and acetylene (10 to 1 by volume) is passed over the catalyst at a space rate of 30 cu ft (STP) per hr per lb catalyst mixture. The temperature of the salt bath is maintained above 450°F.

The gases leaving the reactor (chiefly acetone, hydrogen, and carbon dioxide, with a small amount of acetaldehyde) go to a condenser and thence to a water scrubber. The condensate and the liquid effluent from the scrubber are mixed to yield a 10 per cent aqueous acetone solution, which is rectified in conventional stills. Acetaldehyde is recovered as a by-product.

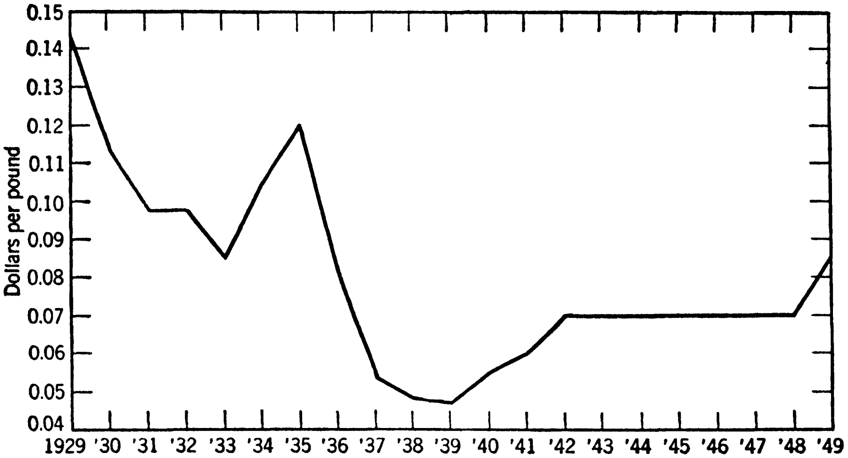
Catalyst life is short, but actual life figures are not available.



Production—Acetone

Use Pattern

	1947 (est.), per cent
Cellulose acetate	50
Chemical manufacture	15
Paint, varnish, and lacquer	10
Solvent for acetylene	5
Drugs	5
Miscellaneous and export	15
	100



Price—Acetone

Miscellaneous

Properties. Colorless, volatile, highly flammable liquid with an ethereal odor.

Mol. wt.	58.08	M.P.	−95.1°C
Sp. gr.	0.791 20°C/20	B.P.	56.5°C

Weight per gallon 6.58 lb (20°C)

Soluble in all proportions with water, alcohol, and ether at room temperature. Slightly soluble in chloroform.

Flash point (open cup)	15°F
Ignition temperature	1,118°F
Vapor density (air = 1)	2.0
Explosive limits (% by volume in air)	Lower 2.15 Upper 13.0

Grades. USP (99 per cent), C.P. (99.5 per cent), and technical.

Containers and Regulations. Tank cars, drums, cans, and bottles. Acetone is classified as a flammable liquid and requires a red ICC shipping label.

Economic Aspects

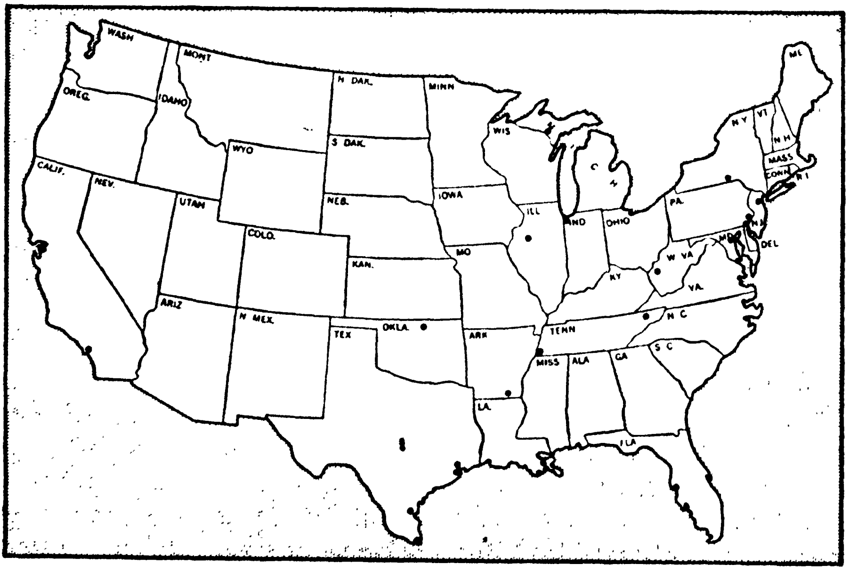
For many years, the principal source of acetone was the dry distillation of calcium acetate, a product of the wood-distillation industry. However, large demands for acetone as a solvent for British cordite in World War I led to the establishment of the fermentation process described previously in which butanol is formed as a joint product. Later, with the development of a commercial process for the hydration of propylene to isopropyl alcohol, it was only natural that a process was devised to manufacture acetone by dehydrogenation of the alcohol.

Today, a small amount of acetone is recovered as a by-product of the Badger-Stafford wood-distillation process, but none is derived from calcium acetate distillation. A strong competitive situation exists between fermentation and petroleum acetone, with the strength of the former existing in a demand for the joint product, butanol, and of the latter in the advantages of cheap raw material and a simple process. Currently, fermentation acetone represents less than 15 per cent of total acetone production. The recently developed process in which acetone is obtained directly from acetylene is indicative of the rising importance of acetylene chemistry. The plant using the process is said to have a capacity of 300 tons per month.

Most of the users of acetone take advantage of its solvent properties. The major chemical use is for the manufacture of ketene, a large portion of which is converted to acetic anhydride.

Actual plants have annual capacities varying between 10,000,000 and 40,000,000 lb. Smaller plants could not take advantage of construction and operation economies inherent in plants of this size.

A further discussion of the economic factors concerning the fermentation process appears under *Butanol.* For a general discussion of fermentation products versus synthetic products from petroleum, see *Ethyl Alcohol.*

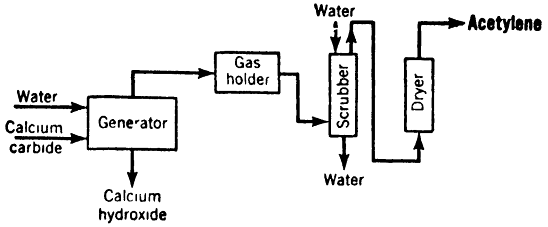


Location of Acetone Plants

ACETYLENE

CH≡CH

From Calcium Carbide



Reaction

$$CaC_2 + 2H_2O \rightarrow CH{\equiv}CH + Ca(OH)_2$$

93–95% yield

Material Requirements

Basis—1,000 cu ft acetylene

Calcium carbide (85%)	218 lb
Water	1,800 lb

Process

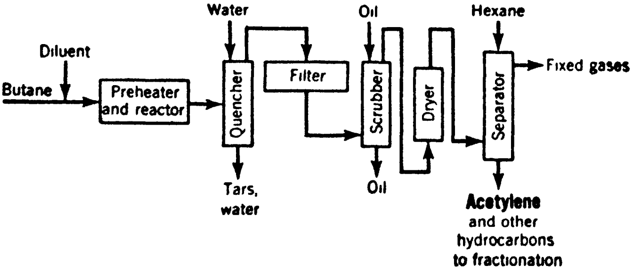
Calcium carbide is formed when lime (essentially free of phosphates and magnesium carbonate) and coke (with low ash content), mixed in a ratio of 60 to 40, are heated to a temperature of 2,000 to 2,100°C in an electric furnace. The reaction is: $CaO + 3C \rightarrow CaC_2 + CO$. The carbon monoxide may be recovered and used as a fuel in lime kilns or as a raw material for chemical synthesis. The liquid calcium carbide is allowed to cool and solidify for 24 to 48 hr and is then crushed and screened for size. The grinding operations are carried out in an atmosphere of nitrogen to prevent explosion from acetylene generated by moisture in the air. The approximate requirements per ton of carbide are: lime (1,982 lb), coke (1,365 lb), electrode paste (33–40 lb), electricity (2,900 kw-hr), and labor (4.6 man-hr). The carbide so produced is about 85 per cent CaC_2; 1 lb of carbide yields 4.5 to 4.7 cu ft acetylene.

There are two standard methods for the production of acetylene from calcium carbide and water: the wet process and the dry process. The wet process consists of adding the carbide to a relatively large quantity of water releasing acetylene gas while the calcium hydrate residue is discharged in the form of a lime slurry containing approximately 90 per cent water.

In order to eliminate the waste of calcium hydrate, the dry process was originated where a limited amount of water (1 to 1 by weight) is added to calcium carbide in a generator. The heat of reaction (166 Btu per cu ft acetylene generated) is employed to vaporize the excess water over the chemical equivalent, leaving a substantially dry calcium hydrate suitable for re-use as a lime source. The temperature must be carefully controlled since acetylene polymerizes to form benzene at 600°C and violently decomposes at 780°C, and air mixtures may explode at 480°C. Generators of both types are usually designed to operate below 300°F and 15 psi.

The crude gas (containing traces of hydrogen sulfide, ammonia, and phosphine) from the generator is either scrubbed with water and caustic-soda solution or led to a purifier where the impurities are absorbed by the use of iron oxide or active chlorine compounds. The dry gas is fed to cylinders or manufacturing units

From Paraffin Hydrocarbons by Pyrolysis



Reaction

$$C_4H_{10} \xrightarrow{\text{Steam}} CH\equiv CH + C_2H_4 + CH_4 + CO + H_2$$

$$C_2H_4 \longrightarrow CH\equiv CH + H_2$$

$$2CH_4 \longrightarrow CH\equiv CH + 3H_2$$

50% yield

Material Requirements (Major)

Basis—1,000 cu ft acetylene

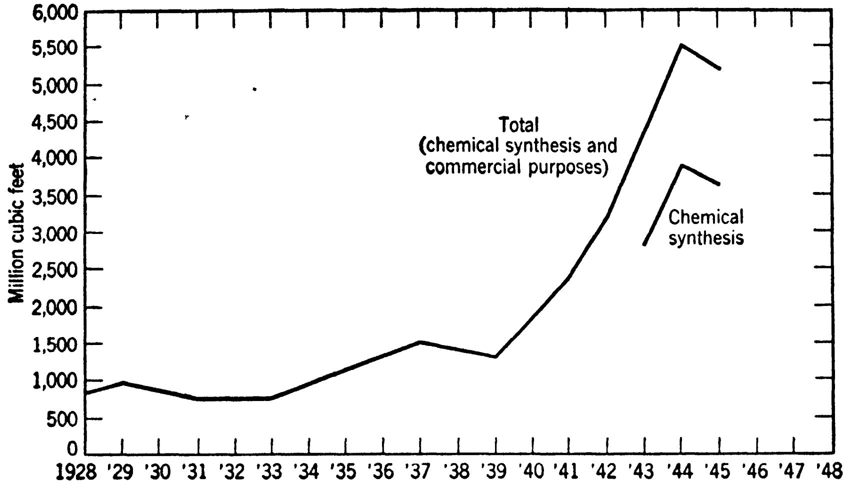
Butane	955 cu ft
Steam (direct)	280 lb

Process

Acetylene may be produced by the thermal decomposition of certain hydrocarbons such as methane, ethane, propane, butane, ethylene, natural gas, or mixtures thereof (Wulff process).

Butane, for example, may be mixed with a diluent such as steam in a 1-to-8 ratio and preheated to about 850 to 900°C. The butane–diluent mixture enters the preheater (metal or metal alloy) at about atmospheric pressure or less and expands two to three times on heating. When the gas passes through the reaction zone (constructed of Carborundum checker work) maintained at approximately 1,300°C, the expansion of the gas is 3.7 to 5, and the residence period is less than 0.1 sec. The cracked gas, analyzing about 12 per cent acetylene, 22 per cent ethylene, and 29 per cent methane (by volume), is rapidly quenched in either a water or an air quencher. The tails from the quencher consist of condensed diluent (water) and traces of tarry by-products. The moist gas is filtered to remove solid particles, scrubbed with oil (such as straw oil), dried, and sent to the separators. The separation of acetylene from paraffin and olefin hydrocarbons is a difficult process, and numerous methods have been proposed such as gas liquefaction or rectification, absorption, scrubbing, and washing with selective solvents. Acetylene may be separated from ethylene and methane by washing with a selective solvent such as hexane at −80°C. The dissolved gases are recovered in two stages, by warming the solution first to −12°C to remove methane and then to a higher temperature to evolve ethylene and acetylene together with some hexane vapor. The latter mixture is fractionated at about −70°C under 2 atm pressure to yield acetylene of 97 to 99 per cent purity. The ethylene and methane may be recycled by mixing with fresh butane, and the cracking process may be repeated. When ethylene and methane are recycled, the yield of crude acetylene based on the volume of butane fed is 50 per cent. Without recycling the yield is 27.5 per cent on the same basis. In German practice, discovered just after the war, acetylene was scrubbed from attendant gases with water under 300 psi, under which conditions olefins were not absorbed.

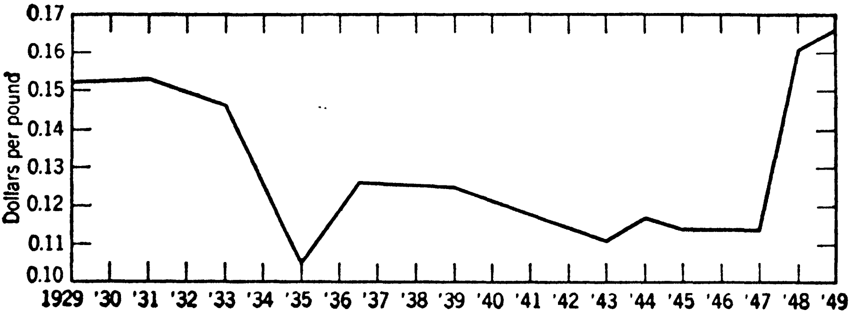
With slight modifications in temperature, pressure, dilution, expansion, and time of reaction, any of the afore-mentioned hydrocarbons may be cracked by this process. The yields from natural gas and propane are about 20 to 30 per cent. Generally, there is a 10 per cent loss on purification to give a product of better than 97 per cent purity.



Production—Acetylene

Use Pattern

	1948 (est.), per cent
Chemicals (acetaldehyde, chlorinated solvents, vinyl compounds, neoprene, acrylonitrile)	75
Welding and lighting	25
	100



Price—Acetylene

Miscellaneous

Properties. Colorless, flammable gas, odorless when pure, but ordinarily has a garlic-like odor because of impurities.

Mol. wt.	26.04	F.P.	−81.8°C
Sp. gr.	0.613 (−80°C) liquid	B.P.	−83.6°C

One pound of acetylene is equivalent to 14.5 cu ft. Soluble in acetone (2,500 cc gas per 100 g, 30,000 cc gas per 100 g at 12 atm), alcohol (600 cc per 100 g), water (100 cc per 100 g), and liquid ammonia at room temperature.

Flash point	Gas
Ignition temperature	635°F
Vapor density (air = 1)	0.91
Explosive limits (% by volume in air)	Lower 2.3 Upper 80

Grades. Technical, 97 to 99 per cent.

Containers and Regulations. Steel pressure cylinders containing 100 to 125 cu ft or 250 to 300 cu ft acetylene. Mixtures of air and acetylene, as well as liquid acetylene, are highly explosive. The cylinders must therefore contain a suitable solvent (such as acetone) and generally a porous material (such as asbestos, kapok, or diatomaceous earth) on which the solution is impregnated. The cylinder pressure must not exceed 250 psi at 70°F, and a red ICC shipping label is required.

Acetylene is produced on the spot where needed by means of portable generators utilizing calcium carbide. Miners' lamps are examples of small generators.

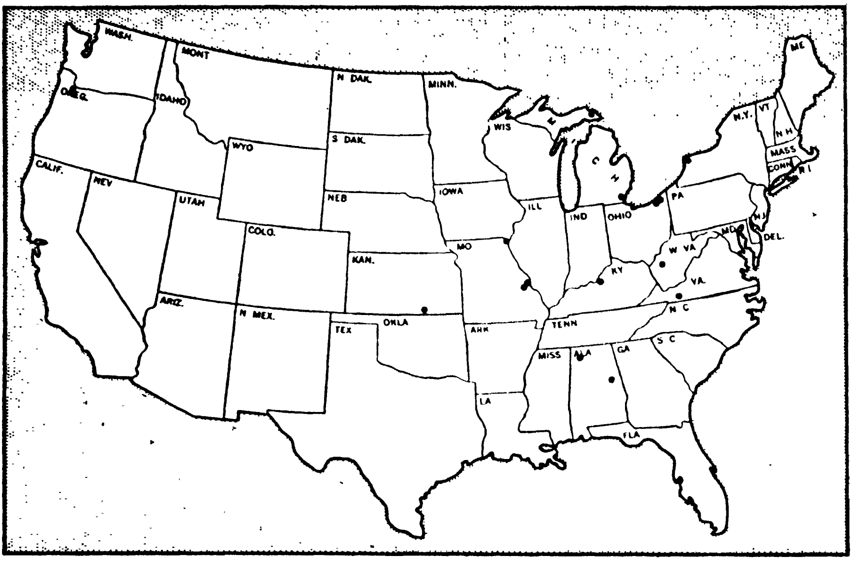
Economic Aspects

It is only in recent years that acetylene has been a chemical raw material of importance. Before World War II it was used largely as a welding and lighting gas. Its large use as a chemical raw material began with acetic acid and was followed rapidly by its use in the manufacture of chlorinated hydrocarbons, vinyl compounds, and neoprene.

One of the chief hindrances to large uses of acetylene is the explosion hazard under even very mild pressure; above 2 atm it detonates rapidly. It is usually handled in cylinders containing felt pads in which it is dissolved in acetone, in which case acetylene can be compressed to 10 to 15 atm. During World War II it was found that, if sufficient water or other diluent were present, it could be handled with safety and dispatch under higher pressures. In fact, it was this knowledge that allowed Nazi Germany to build up a complete synthetic-organic-chemical industry based on acetylene. It is doubtful, however, that very many of the German developments will become equally important in the United States because of competition with various olefins derived from petroleum.

Practically all acetylene is made by the treatment of calcium carbide with water. Great care must be exercised in its preparation, and the history of acetylene generation is fraught with many disastrous explosions.

During World War II when electric power was very short, numerous alternative processes were studied on a pilot-plant scale. The most promising of these were the Wulff process described previously and the Schoch process in which acetylene was produced by the action of a silent electric discharge on methane. It is quite probable that the former process or other hydrocarbon cracking processes will become commercial in the near future, and the development will certainly bear watching during the next few years. The chief advantage of the Schoch process is that equipment can be built as economically on a small as on a large scale. Both the Wulff and Schoch processes produce dilute acetylene gases from which commercial acetylene must be recovered.



Location of Calcium Carbide Plants

The economic smallest-size carbide furnace has a capacity of 2,500 tons of carbide annually, which is equivalent to 800 tons of acetylene. Most plants vary in capacity from 10,000 to 100,000 tons of carbide (3,200 to 32,000 tons of acetylene) per year. A complete carbide plant for manufacturing 20,000 tons of acetylene per year costs approximately $150 per annual ton of acetylene, of which acetylene generation is less than 10 per cent of the total cost.

An economic-size Wulff unit would produce 1,000 tons of acetylene per year plus an equivalent amount of ethylene. A 10,000-ton plant operating on propane as a raw material would probably cost about $175 per annual ton of acetylene produced.

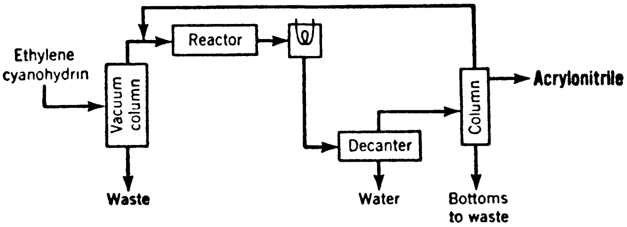
A great many portable generators are operated by those using acetylene for welding. Generators in central plants normally take a charge of 350 lb of calcium carbide, which is equivalent to 115 lb of acetylene (1,650 cu ft under ordinary conditions). Portable generators are available with carbide capacities as low as 15 lb.

ACRYLONITRILE

(VINYL CYANIDE)

$CH_2{=}CHCN$

From Ethylene Cyanohydrin



Reaction

$$CH_2(OH)CH_2CN \xrightarrow{\text{Catalyst}} CH_2{=}CHCN + H_2O$$

90% yield

Material Requirements

Basis—1 ton acrylonitrile (99%)

Ethylene cyanohydrin	2,950 lb
Catalyst	Small

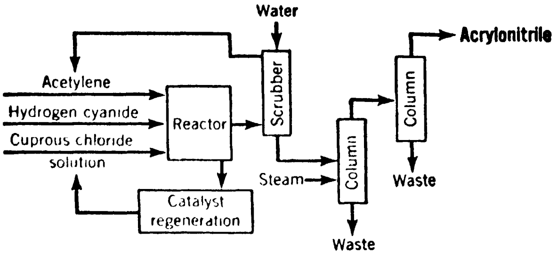
Process

Acrylonitrile is generally manufactured by dehydrating ethylene cyanohydrin, which in turn may be produced by the reaction of ethylene oxide and hydrogen cyanide.

Ethylene cyanohydrin is refined by vacuum distillation and then continuously passed over a dehydration catalyst, such as activated alumina. The reaction may be carried out at either atmospheric or reduced pressure in the vapor phase between 250 and 350°C or in the liquid phase. The reaction products are condensed and passed into a decanter where the water layer is separated and discarded.

The crude acrylonitrile layer is charged into a fractionating column, which yields low-boiling heads that are returned to the ethylene cyanohydrin still. The bottoms consist of high-boiling impurities and are generally discarded. Substantially dry acrylonitrile of 99 per cent purity is obtained from the middle of the column and is sent to storage.

From Acetylene and Hydrogen Cyanide



Reaction

$$C_2H_2 + HCN \xrightarrow{\text{Catalyst}} CH_2{=}CHCN$$

80% yield

Material Requirements

Basis—1 ton acrylonitrile (99%)

Acetylene	1,200 lb
Hydrogen cyanide	1,200 lb
Catalyst loss (contained copper)	Small

Process

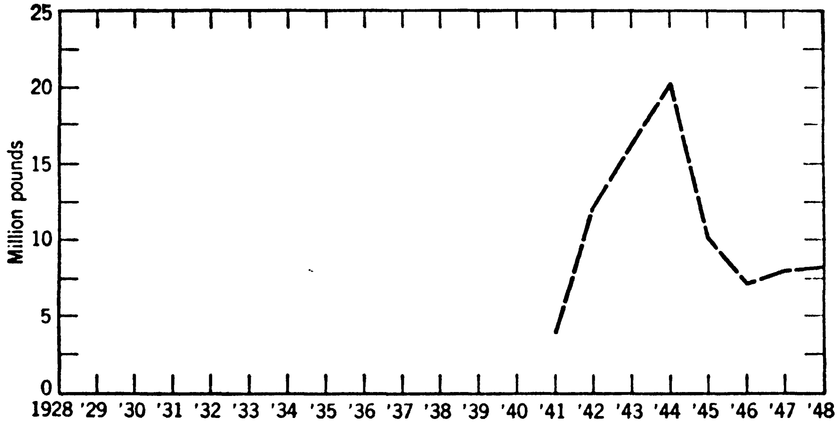
Acrylonitrile is produced by the reaction of acetylene and hydrogen cyanide in the presence of a catalyst under either liquid- or vapor-phase conditions.

Acetylene and hydrogen cyanide in a molar ratio of 10 to 1 are fed into a rubber-lined cylindrical reactor which is kept about two thirds full of catalyst solution. The aqueous solution contains 26 per cent cuprous chloride (based on the weight of dissolved copper). The catalyst may be used to produce approximately 20 lb of acrylonitrile per lb of dissolved copper before regeneration. This may be conveniently accomplished by precipitating the copper with zinc and reconverting to cuprous chloride. The aqueous catalyst solution is maintained at a temperature of 70°C, and the reactor is operated at essentially atmospheric pressure.

The reaction gases from the top of the reactor contain acrylonitrile, unreacted acetylene, 1 to 3 per cent hydrogen cyanide, and small amounts of numerous by-products such as acetaldehyde, vinylacetylene, divinylacetylene, vinyl chloride, cyanobutadiene, lactonitrile, and chloroprene. The gases are washed countercurrently with water in a scrubber which removes the acrylonitrile, hydrocyanic acid, and some of the by-products. The washed gases are recycled to the reactor.

The water solution, containing about 1.5 per cent acrylonitrile, is steam-distilled in a column to give 80 per cent acrylonitrile. The crude product is fractionated in a series of columns to yield 99 per cent pure acrylonitrile. The yield based on acetylene is about 80 per cent and is somewhat higher based on hydrocyanic acid.

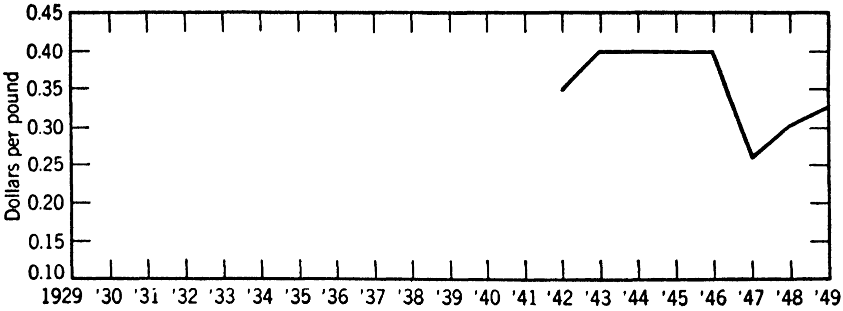
The vapor-phase process involves passing a mixture of equal volumes of acetylene and hydrogen cyanide over a fixed metallic cyanide catalyst (suspended on an inert carrier) at temperatures of 400 to 500°C. The gaseous reactants may be diluted with steam or inert gases to improve the yield, but it is still reported to be rather low. The addition of an acidic substance, such as phosphoric acid, to the crude reaction product entering the column is said to reduce secondary reactions and increase the yield of acrylonitrile.



Production—Acrylonitrile (Estimated)

Use Pattern

	1948 (est.), per cent
Synthetic rubber	85
Miscellaneous	15
	100



Price—Acrylonitrile

Miscellaneous

Properties. Colorless, flammable, mobile liquid with a mild odor.

Mol. wt.	53.06	M.P.	−82°C
Sp. gr.	0.8065 20°C/4	B.P.	78.5°C

Weight per gallon 6.7 lb (20°C)

Soluble in alcohol, ether, carbon disulfide, and most organic solvents. Slightly soluble in water (6 g per 100 ml).

Flash point (open cup)	32°F
Ignition temperature	898°F
Vapor density (air = 1)	1.83
Explosive limits (% by volume in air)	Lower 3.05 Upper 17.0

Grades. Technical (99 per cent).

Containers and Regulations. Tank cars, steel drums, and bottles. Red ICC shipping label required.

Economic Aspects

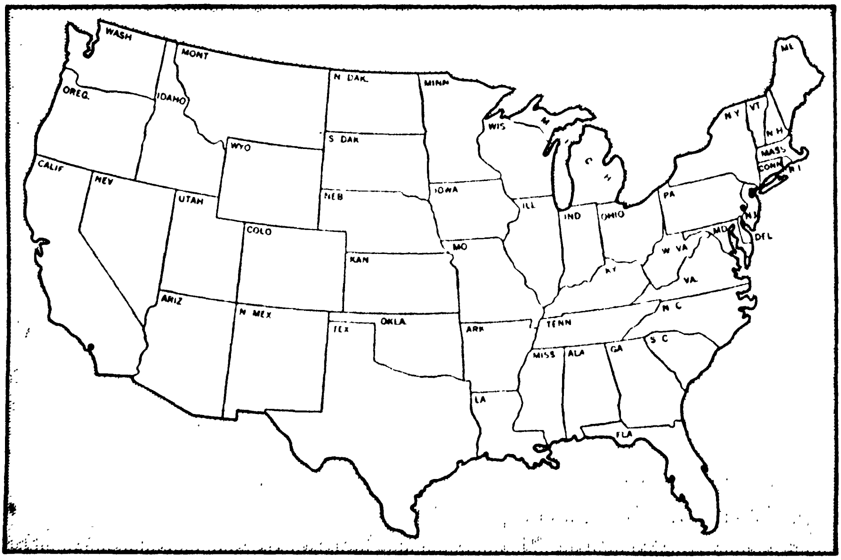
Acrylonitrile is used practically entirely in the manufacture of synthetic elastomers of the Buna N type. In the Government rubber program during World War II, Buna N rubber played only a very minor role, primarily because it was neither a general-purpose elastomer nor paramount for an essential use that could not be partly filled by an elastomer that could be made more easily. Furthermore, part of the equipment required for acrylonitrile manufacture was also adaptable for the manufacture of methyl methacrylate, which was badly needed in the manufacture of aircraft components.

In general, the Buna N synthetic elastomers are superior to other synthetics in resistance to oils and aliphatic hydrocarbons but are much more difficult to mill during compounding. The chief uses of the material may be expected to be in the manufacture of gaskets, packing, seals, automobile parts, gasoline hose, and oil-resistant sheeting. Oil resistance varies with the amount of acrylonitrile in the copolymer. On the other hand, the cold crack temperature becomes higher as the percentage of acrylonitrile is increased.

The presence of both an ethylenic linkage and a cyanide group in the same molecule may make acrylonitrile a useful intermediate in organic-chemical manufacture. Judging from the amount of research work on the subject, future outlets for acrylonitrile may be in the use of its polymers in the manufacture of plastics and synthetic fibers. Two such fibers, one a polyacrylonitrile and the other a copolymer with vinyl chloride, are expected to be offered in the near future. This outlet could be quite large and could result in much cheaper acrylonitrile, which in turn could result in expanded use of Buna N.

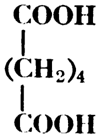
Most acrylonitrile is made from ethylene cyanohydrin at present, but the acetylene process appears competitive. Plants are comparatively small, ranging in size from 200 to 3,000 tons per year. The larger plants cost about $100 to $125 per annual ton production. Since the war, however, the situation has changed as regards plant size. The sole producer has a plant of more than 12,000 tons annual capacity.

There are reports that some acrylonitrile has been made by the catalytic oxidation of allylamine.



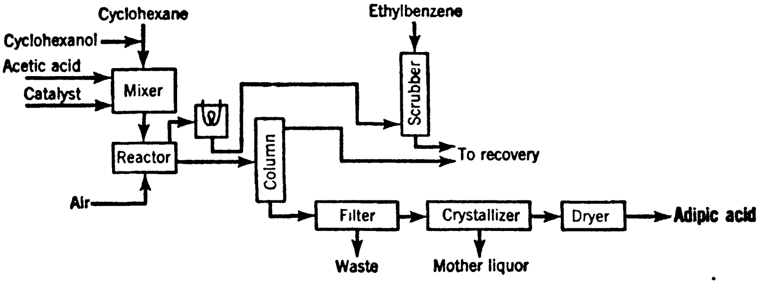
Location of Acrylonitrile Plants

ADIPIC ACID



$$\begin{array}{c} COOH \\ | \\ (CH_2)_4 \\ | \\ COOH \end{array}$$

From Cyclohexane by Oxidation



Reaction

$$C_6H_{12} + 2\tfrac{1}{2}O_2 \rightarrow HOOC(CH_2)_4COOH + H_2O$$

50-70% yield

Material Requirements (Theoretical)

Basis—1 ton adipic acid

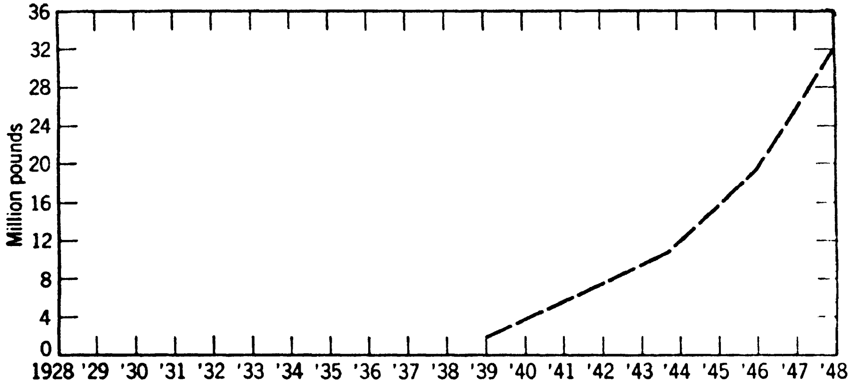
Cyclohexane	1,150 lb	Air	1,100 lb

Process

Adipic acid may be produced by the nitric acid or air oxidation of cyclohexane, cyclohexanol, and cyclohexanone. These raw materials may be obtained from petroleum or made synthetically from benzene or phenol.

Cyclohexane is obtained directly from petroleum by fractionating higher natural-gasoline cuts. Other cuts may be hydroformed to yield a mixture of cyclohexane and methyl cyclopentane. After separation, the latter is isomerized to yield cyclohexane. This material is also made synthetically by hydrogenating benzene. The cyclohexane that results from any of these sources may be used directly as a raw material for adipic-acid manufacture or may be converted to the ketone or alcohol. Liquid-phase oxidation, using air in the presence of a catalyst (such as cobalt acetate), yields 90 per cent of cyclohexanone and cyclohexanol. The latter may also be produced by hydrogenating phenol in the liquid phase at 175°C, using a nickel contact catalyst.

Any or all of these saturated aromatics serve as a raw material for production of adipic acid. For example: Cyclohexane and cyclohexanone are charged into a mixing tank with acetic acid and catalyst. The mixture, containing about 850 parts of cyclohexane, 20 parts of cyclohexanone, 500 parts of acetic acid, 1 part of hydrogen chloride, and 0.7 part of cobalt hexahydrate, is charged into a tantalum-lined reactor. The mixture is heated to about 95°C, and air is charged to the unit until the pressure reaches 150 psi. Air is then bubbled through the mixture at a vigorous rate while the pressure is maintained at 150 psi and the temperature between 95 and 120°C. The exit gases are passed through condensers and then through an ethylbenzene scrubber (cold) to remove cyclohexane vapor.



Production—Adipic Acid (Estimated)

The reaction mixture is discharged into a still where unreacted cyclohexane is recovered for re-use by distillation. The acetic acid is distilled for recovery. The residue is steam-distilled to recover cyclohexanone and cyclohexanol.

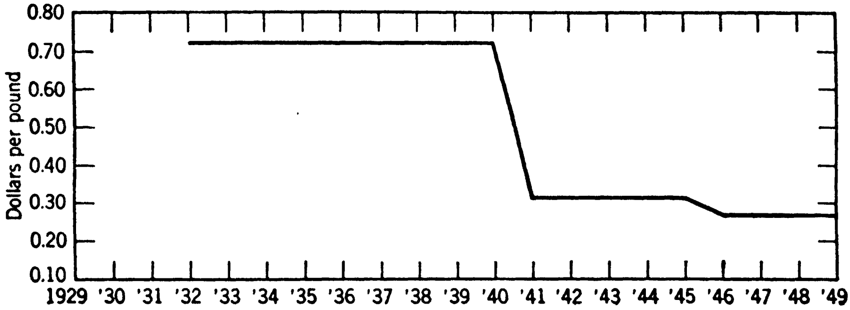
The nonvolatile aqueous mixture of esters, lactones, and dibasic acids is further steam-distilled after a small amount of sulfuric acid has been added to aid hydrolysis. The sulfate ion is removed with a soluble barium salt, and the residue is filtered.

The clear filtrate is run to a crystallizer where crystals of adipic acid separate and are centrifuged and dried. A yield of 50 to 70 per cent based on cyclohexane is realized.

As stated previously, nitric-acid oxidation of cyclohexane–cyclohexanol–cyclohexanone mixtures also yields adipic acid. One difficulty is the simultaneous formation of nitrocyclohexane. The latter material may be air-oxidized to adipic acid, however, and so a two-step process, for example, nitric-acid oxidation followed by air oxidation, has been patented. In all cases, recovery of high-purity adipic acid is complicated by by-products such as succinic, glutaric, *n*-valeric, and *n*-caproic acids.

Use Pattern

	Per cent
Nylon	99
Other	1
	100



Price—Adipic Acid

Miscellaneous

Properties. Colorless to yellowish crystals or crystalline powder.

Mol. wt.	146.14	M.P.	152°C
Sp. gr.	1.360 20°/4	B.P.	265°C$^{100\ mm}$

Soluble in alcohol and ether. Slightly soluble in water (1.4 g per 100 ml at 15°C).

Flash point (closed cup)	385°F
Vapor density (air = 1)	5.04

Grades. Technical.

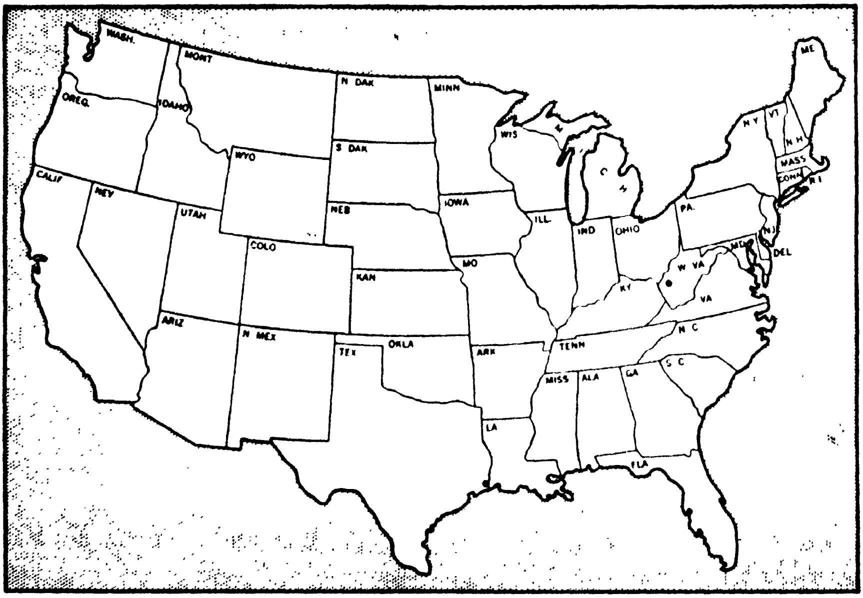
Containers and Regulations. Barrels, tins, and bottles. No ICC shipping label required.

Economic Aspects

It is well known that a commercial process for the manufacture of adipic acid was developed because of demand for the acid in the manufacture of nylon. According to the nylon patents, a wide variety of dibasic acids other than adipic are suitable for nylon manufacture. It is to be assumed, however, that cost, available raw materials, and quality of product favor adipic acid over other dibasic acids. For this reason, increased production of adipic acid is expected. Some competition for nylon may be expected from other comparatively new fibers, but no actual replacement has as yet entered the field. Perhaps the greatest competition will come from the new polyacrylonitrile fiber, Orlon.

Present nylon plants are said to have annual capacities of 8,000,000 lb each, which would mean a calculated requirement of 4,000,000 lb adipic acid annually for each nylon plant. No information is available as to the minimum size of an economic plant.

It is not improbable that furfural may replace benzene and cyclohexane as the raw material for adipic acid, as it has replaced benzene for the manufacture of the other nylon intermediate, hexamethylenediamine (see *Furfural*). An intermediate in hexamethylenediamine production is adiponitrile, which may readily be hydrolyzed to adipic acid. Recently a process has been developed for the manufacture of adipic acid from butadiene, which process is said to have many inherent economies over those processes mentioned previously.



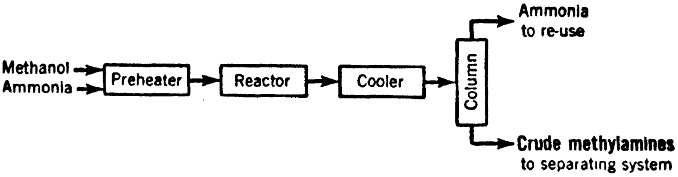
Location of Adipic-Acid Plants

ALKYLAMINES

	Mono-	Di-	Tri-
Methylamine	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
Ethylamine	$C_2H_5NH_2$	$(C_2H_5)_2NH$	$(C_2H_5)_3N$
Isopropylamine	$(CH_3)_2CHNH_2$	$[(CH_3)_2CH]_2NH$	$[(CH_3)_2CH]_3N$
Butylamine	$C_4H_9NH_2$	$(C_4H_9)_2NH$	$(C_4H_9)_3N$
Amylamine	$C_5H_{11}NH_2$	$(C_5H_{11})_2NH$	$(C_5H_{11})_3N$

From Corresponding Alcohol and Ammonia

Example: Methylamine



Reaction

$$CH_3OH + NH_3 \rightarrow CH_3NH_2 + H_2O$$

$$CH_3OH + CH_3NH_2 \rightarrow (CH_3)_2NH + H_2O$$

$$CH_3OH + (CH_3)_2NH \rightarrow (CH_3)_3N + H_2O$$

95% yield (based on methanol)

Conversion (based on ammonia)—13.5% CH_3NH_2

7.5% $(CH_3)_2NH$

10.5% $(CH_3)_3N$

Material Requirements

Basis—1 ton methylamines (mixed)

Methanol	3,000 lb
Ammonia	850 lb

Process

The methylamines are made by reacting methanol and ammonia in a continuous-flow system in the presence of a dehydration catalyst, followed by the separation of unreacted raw materials and the mono-, di-, and trisubstituted methylamines.

Methanol (1 mole) and ammonia (2 moles) are mixed and pumped through a preheater or heat exchanger (at 200 psi), and heated to 350°C. The vapors then pass to a reaction chamber containing an alumina-gel catalyst where amination takes place at about 450°C. Space velocity may vary but is usually kept in the vicinity of 1,000 reciprocal hours. The crude methylamines leaving the reaction chamber contain unreacted methanol and ammonia as well as smaller amounts of by-products (carbon dioxide and formaldehyde).

The reaction mixture passes through a cooler and thence to a rectifying column, operated under reaction pressure (200 psi), in which ammonia is removed as overhead for re-use. An ammonia-free amine mixture leaves the bottom of the column. This mixture contains all three methylamines in proportions depending on the reaction conditions chosen. Under the conditions stated the mixture will be essentially as follows: monomethylamine, 50 mole per cent; dimethylamine, 20 mole per cent; trimethylamine, 30 mole per cent. The boiling points of the three amines are quite close, and hence the amines are difficult to separate by straight fractionation.

The use of azeotropes, such as xylene, has been found of value.

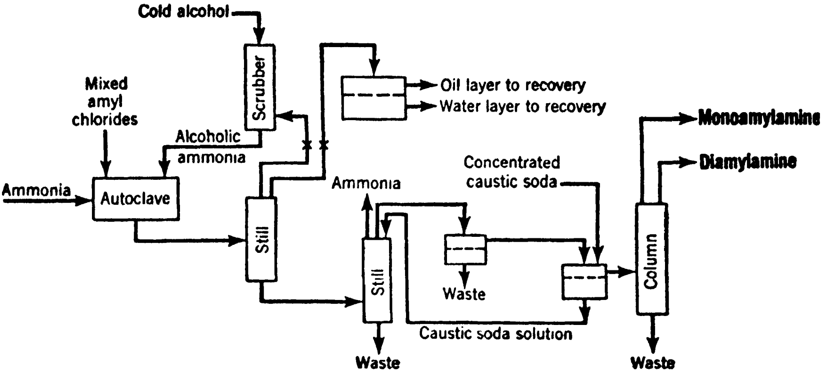
If larger proportions of dimethylamine or trimethylamine are desired, the ratio of these products to monomethylamine may be increased by recycling the lower amine, and by reducing the ammonia–methanol ratio. Usually monomethylamine is the most desirable product, and so either water or trimethylamine is added to the feed to reduce formation of di- and trimethylamines.

Higher Amines. The higher amines, ethyl- through amyl-, may also be made by processes similar to that described for the methylamines. Either dehydration catalysts (such as alumina) or hydrogenation catalysts may be used, the latter in conjunction with hydrogen. When hydrogenation catalysts, such as nickel are used, which are susceptible to high temperatures, the reaction is run at higher pressures in the liquid phase.

An example of the conditions used in the butylamine process by passing butanol, ammonia, and hydrogen over a hydrogenation catalyst is as follows: catalyst—pelleted nickel; temperature—190°C; space velocity—2,250 reciprocal hours; molar percentage in feed—7.5 per cent butanol, 45 per cent ammonia, 43 per cent hydrogen; over-all conversion—86.3 per cent (24.4 per cent mono-, 46.7 per cent di-, and 15.2 per cent tributylamine). Conversion to butyronitrile is 2.4 per cent. Over-all yield to amines after butanol recovery is 91.6 per cent. When hydrogen is not used in the manufacture of higher amines, a large part of the alcohol is converted to the nitrile.

From Alkyl Chloride and Ammonia

Example: Amylamines



Reaction

$$C_5H_{11}Cl + NH_3 \rightarrow C_5H_{11}NH_2 \cdot HCl$$

$$2C_5H_{11}Cl + 2NH_3 \rightarrow (C_5H_{11})_2NH \cdot HCl + NH_4Cl$$

$$C_5H_{11}NH_2 \cdot HCl + (C_5H_{11})_2NH \cdot HCl + NH_4Cl + 3NaOH \rightarrow$$
$$C_5H_{11}NH_2 + (C_5H_{11})_2NH + NH_3 + 3NaCl + 3H_2O$$

95% yield

Material Requirements

Basis—1 ton amylamines (mixed)

Mixed amyl chlorides	2,500 lb	Caustic soda (solid)	975 lb
Ammonia	360 lb	Ethyl alcohol (loss)	Small

Process

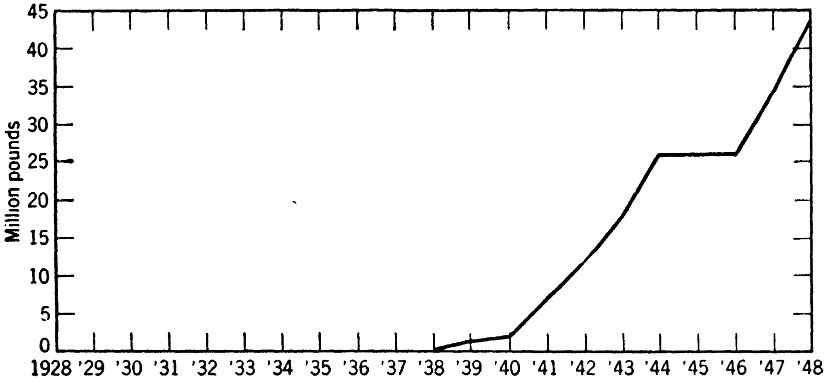
A mixture of alcoholic ammonia and mixed amyl chlorides (distillation—95 per cent between 85 and 109°C) is pumped to an autoclave where it is further mixed with anhydrous ammonia. Temperature of the reacting mixture is maintained at 160 to 165°C for 2 hr, after which the temperature is raised until the autoclave pressure reaches 400 psi, under which conditions the contents of the reactor are held for an additional 2 hr. The pressure is released, and the autoclave contents are discharged to a still operating at a pressure below 7 psi. Here ammonia is recovered through a reflux system attached to a series of scrubbers in which ammonia is recovered in cold alcohol and used for the next batch of amine.

When the ammonia present in the contents of the still has dropped to less than 1 per cent, by-product amylene and amyl alcohols, unreacted amyl chloride and ethyl alcohol, and traces of amines are distilled overhead until the distillate consists only of water. The condensed distillate is mixed with more water, thus forming two liquid layers. The aqueous and oil layers are separated and sent to separate fractionation and recovery systems.

The residue remaining in the still, consisting essentially of amine hydrochlorides, is sent to a second still where a caustic-soda solution is added to liberate the amines from their salts. Some liberated ammonia is then distilled overhead, followed by wet amylamines. On condensation of the amine vapors, most of the accompanying water separates. The oil layer (wet amylamines) is separated in a decanter and pumped to an agitated vessel for dehydration with concentrated caustic soda. The caustic layer is returned to the still for amine liberation, and the dry amylamines go to a rectifying column for fractionation.

The product consists of 3 parts of monoamylamines and 2 parts of diamylamines. Very little of triamylamines is found.

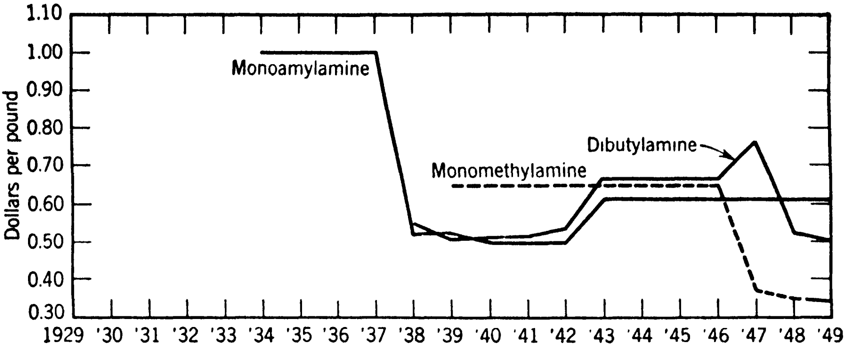
Triamylamines may be made by reacting diamylamines with mixed amyl chlorides and caustic soda in the autoclave mentioned previously for 4 hr at 205 to 210°C. The separation equipment used for mono- and diamylamines may be used to recover triamylamines by steam distillation followed by vacuum fractionation.



Production—Alkylamines

Use Pattern

Chemical intermediate	No breakdown available
Dyestuffs	
Rubber chemicals	
Insecticides	
Synthetic detergents	
Flotation agents	
Corrosion inhibitors	
Solvent	



Price—Alkylamines

Miscellaneous

Properties.

	Mol. Wt.	Sp. Gr.	M.P., °C	B.P., °C	Flash Point, °F (Open Cup)
Methylamines:					
Mono-	31.06	0.699	−92.5	−6.6	10
Di-	45.08	0.680	−96.0	7.4	20.8
Tri-	59.11	0.662 −5°C	−124	3.5	
Ethylamines:					
Mono-	45.08	0.706 0/4	−80.6	16.6	
Di-	73.14	0.705 25/4		55.5	5
Tri-	101.19	0.723 25/4	−114.8	89.5	20
Butylamines:					
Mono-*n*	73.14	0.739 25/4	−50.5	77.8	10
Di-*n*	129.24	0.767 20/4	< −50	161	135
Tri-*n*	185.34	0.778 20/20	< −70	214	175
Amylamines:					
Mono-*n*	87.16	0.761 20/4	−55	104.4	65
Di-*n*	157.29			204	160
Tri-*n*	227.42			240	215

All the listed amines are soluble in alcohol and in ether; all the mono- and diamines are soluble in water except diamylamine; of the trialkylamines only trimethylamine is appreciably soluble in water.

Grades. Monomethylamine and dimethylamine, 100 per cent, and 25 to 40 per cent; other amines, technical.

Containers and Regulations. Tank cars, tanks, drums, cylinders (monomethylamine and dimethylamine, 100 per cent). Red ICC shipping label required for methyl- and ethylamines, monobutyl- and monoamylamines.

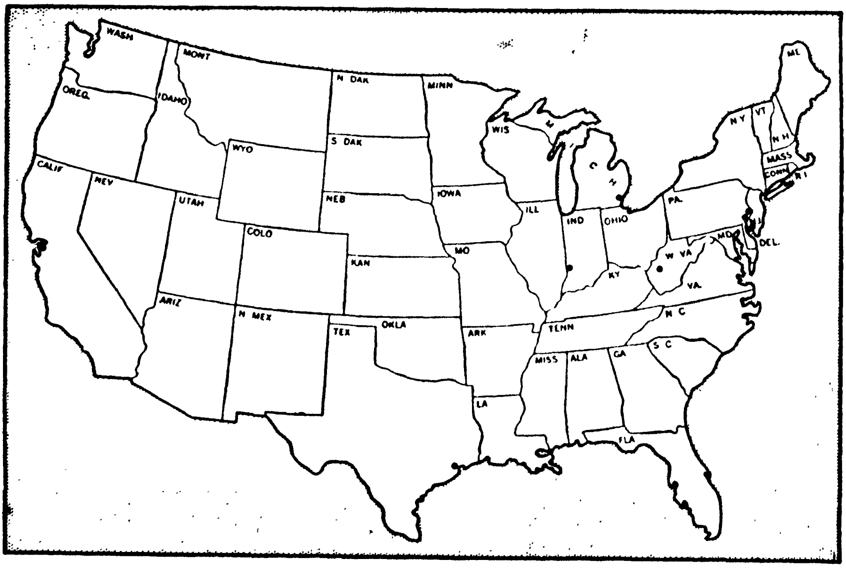
Economic Aspects

The mono-, di-, and trialkylamines ranging from methyl- through amyl- are comparative newcomers to large-scale organic-chemical manufacture. Wartime demands for amines for explosives and as intermediates for rubber accelerators led to increased plant capacity, which in turn has stimulated research on other applications. Present indications are that uses will increase and added production capacity will again be needed.

Most of the new uses will be in the field of organic synthesis, although large quantities could be required as corrosion inhibitors and color stabilizers in gasoline. For strictly amine reactions, the amylamines are preferred because of ease of handling (lower vapor pressure).

The manufacturing processes are of a nature well suited to large-scale production. It is therefore to be expected that plants will be fairly large. The logical manufacturers of the amines are the producers of one or more of the necessary raw materials, for reasons of economy. In most cases, the same equipment is suitable for the manufacture of a number of different alkylamines, which lends flexibility to production.

Plants with annual capacities between 1,000,000 and 5,000,000 lb require an investment between $150 and $225 per 1,000 lb annual capacity, depending on the particular amines to be made and the size of the plant.

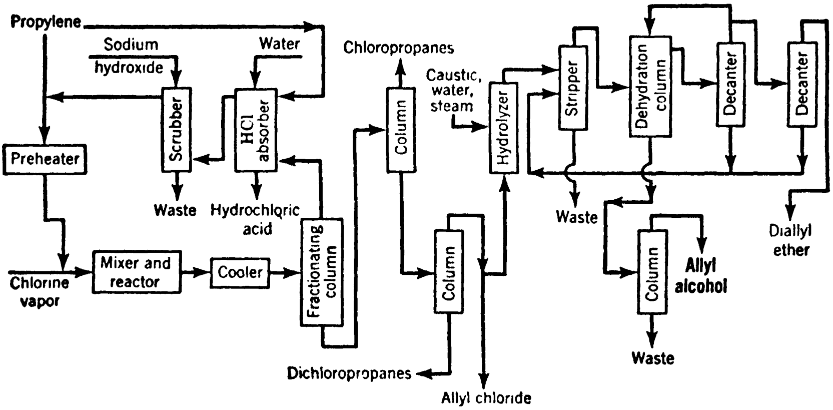


Location of Alkylamine Plants

ALLYL ALCOHOL

$CH_2{=}CHCH_2OH$

From Propylene



Reaction

$$CH_2{=}CHCH_3 + Cl_2 \rightarrow CH_2{=}CHCH_2Cl + HCl$$

$$CH_2{=}CHCH_2Cl + NaOH \rightarrow CH_2{=}CHCH_2OH + NaCl$$

70-80% yield

Material Requirements

Basis—1 ton allyl alcohol (plus 200 lb diallyl ether)

Propylene	2,000 lb	Sodium hydroxide	1,500 lb
Chlorine	3,500 lb	Sodium carbonate	150 lb

Process

The high-temperature continuous chlorination of propylene (obtained by petroleum-cracking processes) yields allyl chloride which may be converted to allyl alcohol by continuous hydrolysis with aqueous sodium hydroxide.

Dry propylene gas is passed through a preheater maintained at about 400°C and is mixed with chlorine in a ratio of 5 moles of propylene to 1 mole of chlorine. The chlorine is previously vaporized by passing the liquid through hot-water heaters. The vaporized chlorine reaches the mixing jet at 60 psi and 20°C. The mixed gases pass from the jet into a steel tube reactor which is insulated for temperature control. The exothermic nature of the reaction increases the temperature of the reaction mixture from about 400°C to 500 to 510°C. The time of residence of the gases in the reaction zone is not too critical and is probably in the range of 2 to 3 sec. The reactor is at a pressure of about 15 psi gage. Utilization of chlorine in the reactor is over 99 per cent. Two reactors are run alternately to allow cleanout of carbon, which is done about once every 2 weeks. Based on the moles of chlorine fed to the reactor, approximately 80 per cent allyl chloride, plus varying amounts of chloropropenes, mixed dichlorides, trichlorides, and heavier residues are obtained. Of these by-products, the cis- and trans-1,3-dichloropropenes and 1,2-dichloropropane occur in largest quantities (*ca.* 15 per cent). One mole of hydrogen chloride is formed with each mole of allyl chloride.

The reaction products are recovered continuously by being passed through a cooler into a fractionating column where the excess propylene and hydrogen chloride are separated from the organic chlorides. Liquid propylene (from storage) is used as reflux, and the top of the fractionator is cooled to about −40°C by self-refrigeration of propylene in a flash drum. The heads from the fractionator are passed into an absorber where hydrogen chloride is recovered as hydrochloric acid of commercial concentration (32 per cent by weight HCl). Liquid propylene is injected into the absorber to remove the heat of absorption, and the propylene leaving the top is scrubbed with aqueous sodium hydroxide. The propylene is then compressed and returned to storage for re-use.

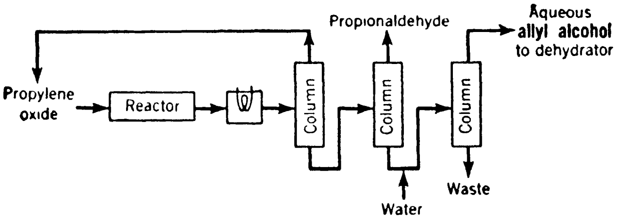
The crude allyl chloride from the bottom of the fractionating column is distilled in two columns. Light ends (mostly 2-chloropropene) and traces of propylene are taken as vapors from the first column, and refined allyl chloride is taken as overhead from the second. The yield based on propylene is about 85 per cent of theoretical. The bottoms, containing mostly dichloropropenes, are sent to storage.

Allyl chloride is fed to a hydrolyzer where the water-insoluble chloride is dispersed in a rapidly circulating stream of dilute caustic. The hydrolyzing medium is made up by the continuous injection of a 20 per cent sodium hydroxide solution, treated with sodium carbonate, and live steam. The hydrolyzer operates at 145 to 155°C and 200 psi, and at a *p*H of 10 to 12. The caustic concentration is about 1.25 normal, which is equivalent to approximately 5 per cent sodium hydroxide. Under these conditions a contact time of from 10 to 15 min is generally used.

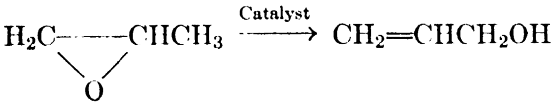
The hydrolyzed product is withdrawn continuously from the top of the reactor and fed directly into a stripper. Live steam is fed into the bottom, and an allyl alcohol–diallyl ether–water mixture is obtained overhead. The bottoms, containing water, salt (sodium chloride), and traces of caustic soda and allyl alcohol are sent to waste. The crude allyl alcohol is refined by distillation and dehydration, diallyl ether being used as the dehydrating agent. The crude product is fed into a dehydration column, where a ternary azeotrope, consisting of about 9 per cent allyl alcohol, 79 per cent diallyl ether, and 12 per cent water, is obtained as overhead at about 78°C. The product is condensed and passed into a phase separator, where the top layer containing about 90 per cent diallyl ether, 9 per cent allyl alcohol, and 1 per cent water is recycled in part, and the remainder is sent into a second decanter. Here it is washed with water to remove the allyl alcohol, and, after settling, the top layer, diallyl ether, is sent to storage. The lower wash-water layer and the bottom layer from the first decanter, containing about 90 per cent water, 10 per cent allyl alcohol, and traces of diallyl ether, is recycled to the crude stripper for alcohol recovery.

The bottom product from the dehydration column is redistilled to yield refined allyl alcohol. The small amounts of high-boiling impurities obtained are discharged from the bottom of the column. The yield of allyl alcohol based on allyl chloride is about 90 per cent, the remainder being mostly diallyl ether.

From Propylene Oxide



Reaction



$$H_2C\underset{\searrow\ O\ \swarrow}{\text{——}}CHCH_3 \xrightarrow{\text{Catalyst}} CH_2{=}CHCH_2OH$$

70–80% yield

Material Requirements

Basis—1 ton allyl alcohol

Propylene oxide	2,650 lb

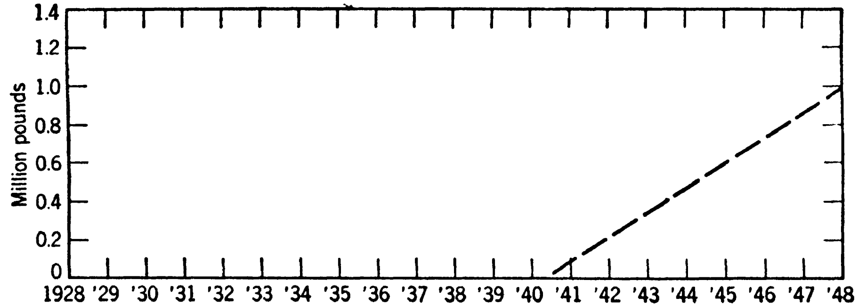
Process

Propylene oxide is converted to a mixture of allyl alcohol and propionaldehyde by vapor-phase isomerization over a lithium phosphate catalyst.

Distilled propylene oxide (distilled to remove traces of chlorine compounds which lower catalyst life) is vaporized and passed through a tubular reactor containing a catalyst consisting essentially of sized particles of lithium phosphate. The reaction is exothermic, and reaction temperature is maintained at 230 to 270°C by control of propylene oxide feed rate and removal of heat from the outside of the reactor tubes by means of a heat-transfer fluid. Space velocity usually varies from 1 to 2 volumes of liquid propylene oxide per volume of catalyst per hour.

The exit gases from the reactor contain allyl alcohol, propionaldehyde, acetone, and unreacted propylene oxide. These products are condensed and then distilled in a series of towers. Overhead from the first column (unreacted propylene oxide) is recycled; propionaldehyde is distilled from a second column. Water may be added in a third column to allow a constant-boiling mixture of allyl alcohol (73 per cent) and water (27 per cent) to distil overhead. The wet alcohol may be dehydrated by distillation in the presence of a suitable withdrawing agent for the water, for example, benzene or diisopropylether.

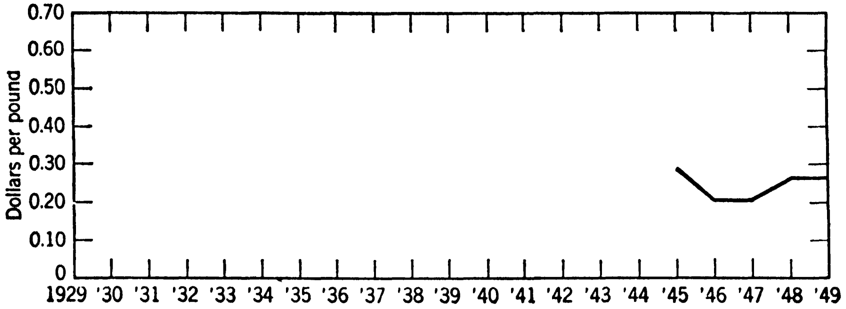
Conversions and yields depend on proper balance of reaction variables. By reacting 20 to 30 per cent of the propylene oxide per pass, allyl alcohol yields of 70 to 80 per cent may be attained. Catalyst activity is maintained by periodic blowing of oxygen over the catalyst at an elevated temperature.



Production—Allyl Alcohol (Estimated)

Use Pattern

Resins and Plasticizers	100 per cent



Price—Allyl Alcohol

Miscellaneous

Properties. Colorless, limpid liquid with a pungent odor.

Mol. wt.	58.08	M.P.	Glass at −190°C
Sp. gr.	0.854 20°C/4	B.P.	96.9°C

Weight per gallon 7.1 lb (20°C)

Soluble in water, alcohol, and ether.

Flash point (closed cup)	70°F
Ignition temperature	713°F
Vapor density (air = 1)	2.00
Explosive limits (% by volume in air)	Lower 2.5 Upper 18

Grades. Technical.

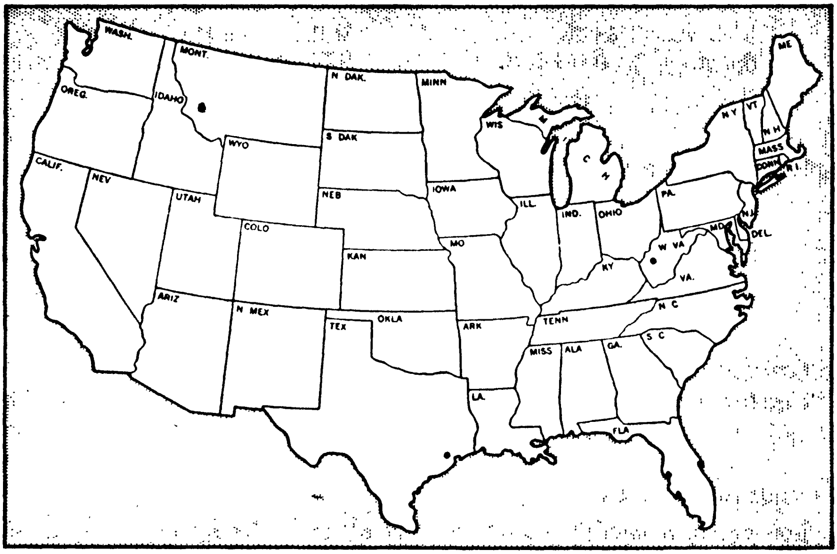
Containers and Regulations. Tank cars, iron drums, and bottles. Requires a red ICC shipping label and "Poison" label.

Economic Aspects

For years, a small amount of allyl alcohol was recovered as a by-product of the wood-distillation industry. The two new synthetic processes described previously were developed in connection with much broader research programs in organic synthesis. The two processes are highly competitive and well protected by patents. Both processes have been commercialized because of possible demands for allyl alcohol for plastics manufacture. Further outlets in both the plastics and coatings industries are being sought, which leads one to believe that production of allyl alcohol will continue to increase. Although there are only two producers at present, the patent literature indicates that another producer may enter the field, using propylene glycol as a raw material.

Commercial-size plants should probably have capacities between 2,000,000 and 10,000,000 lb per yr when demand warrants sufficient production. The capital investment for such plants will range from 60 to 25 cents per annual pound capacity.

Both processes described produce by-products for which an outlet is necessary if the operation is to be economic. Propionaldehyde from the isomerization process finds use as a chemical intermediate whereas ethylene dichloride from the chloride process is in demand as a chlorinated solvent. Another by-product, a mixture of 1,3-dichloropropylene and 1,2-dichloropropane is sold as a soil fumigant. Diallyl ether, a by-product of the allyl chloride process, has few, if any, uses at present. A variation in the chlorination process may lead to propylene chloride, which offers interesting possibilities in organic synthesis. Epichlorohydrin is an interesting intermediate in the chloride process.



Location of Allyl Alcohol Plants

ALUM (CRYSTAL)

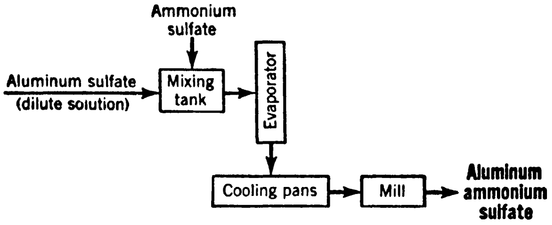
Ammonia alum—$Al_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$ (aluminum–ammonium sulfate)

Potash alum—$Al_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$ (aluminum–potassium sulfate)

Soda alum—$Al_2(SO_4)_3 \cdot Na_2SO_4 \cdot 24H_2O$ (aluminum–sodium sulfate)

From Aluminum Sulfate

Example: Ammonia alum



Reaction

$$Al_2(SO_4)_3 + (NH_4)_2SO_4 + 24H_2O \rightarrow Al_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$$

99% yield

Material Requirements

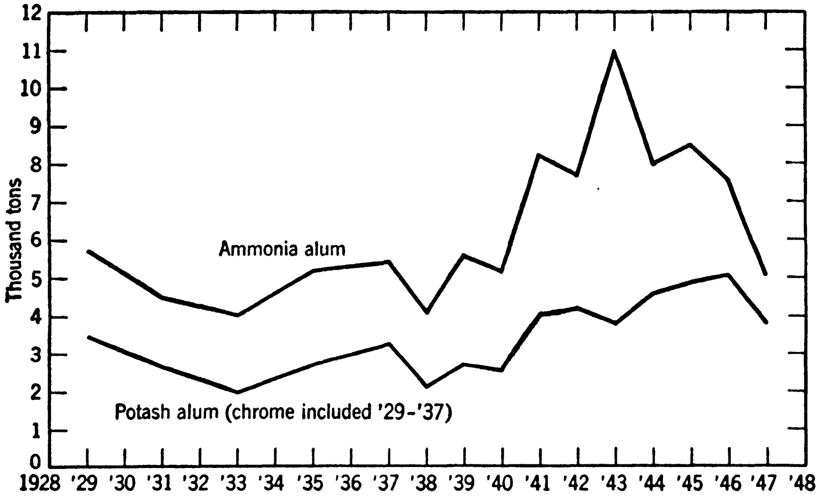
Basis—1 ton ammonia alum

Aluminum sulfate	760 lb
Ammonium sulfate	294 lb

Process

Crystal alums are manufactured in a manner similar to the aluminum sulfate process, and the manufacture entails only one additional step.

A dilute aluminum sulfate solution (35°Bé) is charged into an open, lead-lined evaporator heated by steam coils. The corresponding alkali metal (or radical) sulfate is added in approximately equimolecular amounts. The addition of ammonium sulfate, potassium sulfate, or sodium sulfate will produce ammonia, potash, or soda alums, respectively. The mixed solution is concentrated and then run into cooling pans or tables. The resulting solid cake is broken and ground to uniform size for sale. Yields are practically theoretical based on aluminum sulfate. See *Aluminum Sulfate* for details.

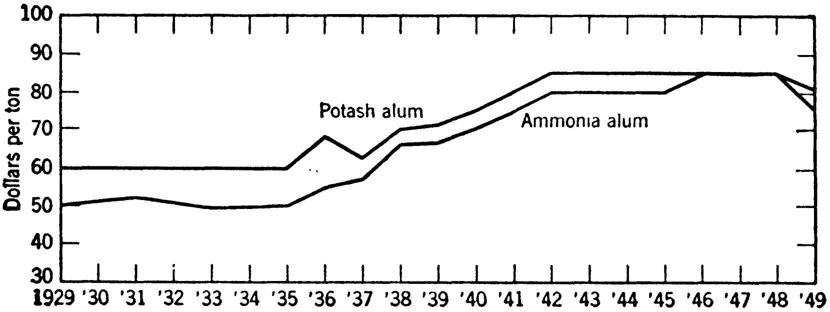


Production—Alum

Data for recent years are taken from Bureau of Mines Statistics. U. S. Census of Manufactures—1947 indicates ammonia alum production for 1947 to be 5,018 short tons, and potash alum production for 1947 to be 23,106 short tons

Use Pattern

Almost same as aluminum sulfate.



Price—Alum

Miscellaneous

Properties. *Ammonia alum.* Colorless crystals having a strong astringent taste.

Mol. wt.	906.4	M.P.	93.5°C
Sp. gr.	1.64 20°C/4	B.P.	Loses $20H_2O$ at 120°C

Soluble in water (3.9 g per 100 g at 0°C, in all proportions at 100°C). Insoluble in alcohol.

Potash alum. White crystals having an astringent taste.

Mol. wt.	948.76	M.P.	92°C
Sp. gr.	1.75 20°C/4	B.P.	Loses $18H_2O$ at 64.5°C

Soluble in water (5.7 g per 100 g at 0°C, in all proportions at 93°C). Insoluble in alcohol.

Soda alum. Colorless, efflorescent crystals with a saline, astringent taste.

Mol. wt.	916.56	M.P.	61°C
Sp. gr.	1.675 20°C/4		

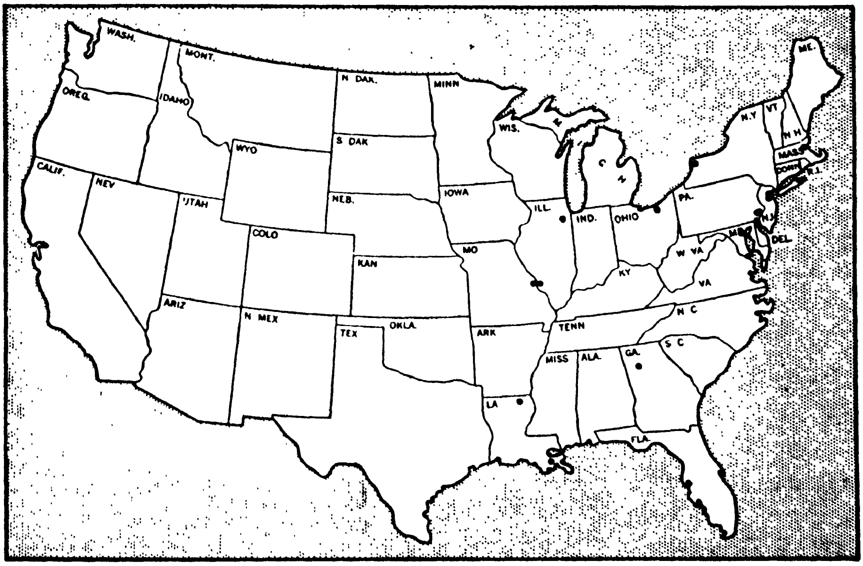
Soluble in water (106.4 g per 100 g at 0°C, 121.7 g per 100 g at 45°C). Insoluble in alcohol.

Grades. Ammonia and potash alum: USP, C.P., and technical (lump, ground, and powdered). Soda alum: Pure crystals, C.P., and technical.

Containers and Regulations. Bulk shipments, barrels, bags, kegs, and bottles. No ICC shipping label required.

Economic Aspects

Correctly speaking, the term "alum" denotes a double sulfate salt of aluminum or chromium with one of the alkali metals or the ammonium radical. Commercially, however, the term "alum," or more usually



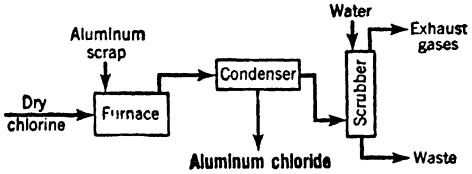
Location of Alum (Ammonium, chrome, potash, sodium) Plants "filter alum," denotes $Al_2(SO_4)_3 \cdot 18H_2O$. The others are known commercially as "crystal alums" and are produced in small quantities compared to filter alum.

All crystal alums are made by the simple addition of the specific alkali sulfate to aluminum sulfate solution followed by crystallization. Some potash alum is made by leaching the mineral alunite. Plant requirements are simple and may be almost any size. The crystal alums (except chrome alum) are usually made by a few aluminum sulfate manufacturers. Chrome alum is usually made by the makers of other chromium chemicals. It is used largely as a high-purity chromium salt in mordanting, in inks, and in printing. Soda alum is used in largest quantities by baking-powder manufacturers.

ALUMINUM CHLORIDE

$AlCl_3$

From Aluminum Metal and Chlorine



Reaction

$$2Al + 3Cl_2 \rightarrow 2AlCl_3$$

Material Requirements (Theoretical)

Basis—1 ton aluminum chloride

Aluminum scrap	400 lb
Chlorine	1,600 lb

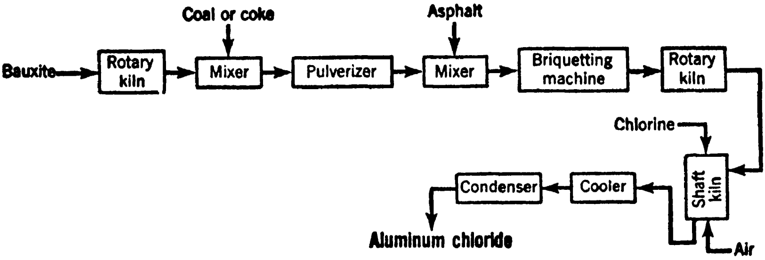
Process

Scrap aluminum, or a mixture of scrap and pig aluminum, is charged to a refractory crucible furnace in which it is melted (660°C). Dry chlorine is passed into the molten charge and forms aluminum chloride, which vaporizes and leaves the furnace through a vapor duct in the top. The vapors are then passed into air-cooled iron condensers where aluminum chloride sublimes below 178°C. The aluminum chloride is removed periodically.

By proper regulation of the chlorine rate, no free chlorine remains in the exit gases from the furnace, but a protective absorber is usually placed beyond the aluminum chloride condenser, to absorb unreacted chlorine and any aluminum chloride that may pass through the condenser.

Purity of the aluminum chloride depends on the quality of the aluminum used and dryness of the chlorine. High-purity aluminum chloride is usually obtained, but even so it is straw-colored because of the presence of traces of ferric chloride.

From Bauxite and Chlorine



Reaction

$$Al_2O_3 + 3C + 3Cl_2 \rightarrow 2AlCl_3 + 3CO$$

Material Requirements (Theoretical)

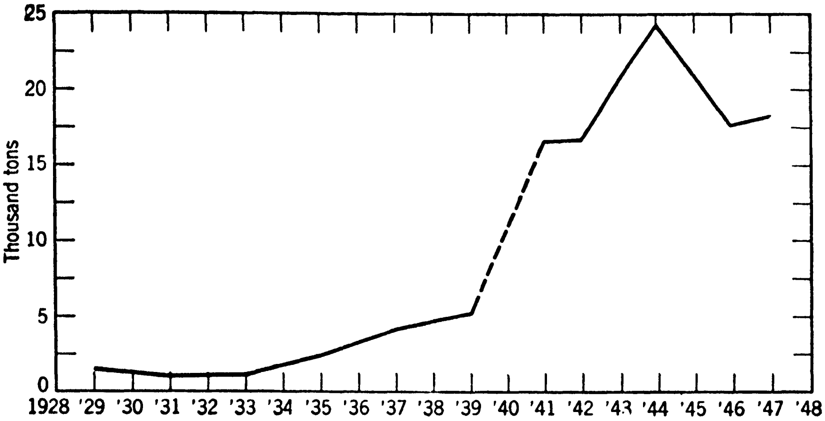
Basis—1 ton aluminum chloride

Bauxite (58% Al_2O_3)	1,325 lb	Chlorine	530 lb
Coke	275 lb	Air	Variable
Asphalt	80 lb		

Process

Crude bauxite (low in iron and silicon) is calcined in a fire-heated rotary kiln at 1,800°F to remove all free and combined water. The dehydrated, calcined bauxite is then mixed with one-half to one-third its weight of coal or coke, and the mixture is finely pulverized. Sufficient asphalt binder is mixed with the powder so that it may be briquetted. The briquets (about 2 lb each) are recalcined in a rotary kiln to drive off the volatile matter in the coal and to produce a calcined product of about 18 per cent carbon.

The hot briquets are charged to a vertical shaft kiln made of iron lined with firebrick. To protect the iron shell from chlorine, a layer of powdered bauxite separates the firebrick and the iron shell. Air is blasted into the briquet-filled furnace at the bottom and half way up and heats the bauxite to 1,600°F in about 15 min. The air blast is stopped, and chlorine is blown in the top of the furnace until the alumina is converted to aluminum chloride. In a 20-ton furnace, the chlorinating period is 8 to 10 hr, during which time aluminum chloride vapors leave the bottom of the furnace and pass through a cooler to a condenser where the chloride sublimes and is removed periodically.

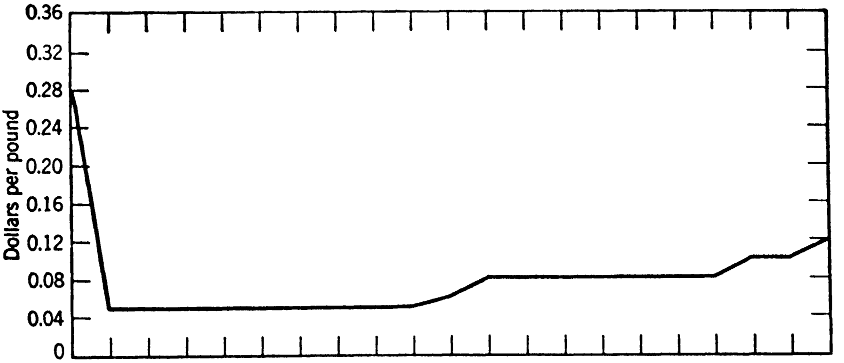


Production—Aluminum Chloride (Anhydrous and crystal as such since 1941; all grades as 100% $AlCl_3$ 1929–39)

Data for years 1941 to 1947 are taken from Bureau of Mines Statistics. U. S. Census of Manufactures—1947 shows total aluminum chloride production in 1947 to be 232,263 short tons

Use Pattern

	1948 (est.), per cent
Petroleum (refining and catalyst)	50
Dyes	30
Miscellaneous	20
	100



Price—Aluminum Chloride

Miscellaneous

Properties. Anhydrous—white deliquescent hexagonal crystals, which sublime readily.

Mol. wt.	133.34	M.P.	194°C (5.2 atm)
Sp. gr.	2.44 25°C/4	B.P.	182.7°C (752 mm), sublimes at 178°C

Soluble in water (69.87 g per 100 ml at 150°C, decomposes in hot water), ether, chloroform, and carbon tetrachloride. Insoluble in benzene.

The anhydrous form crystallizes from hydrochloric acid as the hexahydrate ($AlCl_3 \cdot 6H_2O$) in the form of colorless deliquescent triagonal crystals.

Grades. Technical anhydrous, technical crystals, crystalline hydrated, C.P. crystals, N.F., 32°Bé solution (35 per cent $AlCl_3$).

Containers and Regulations. Airtight drums and sealed glass vials. No ICC shipping label required.

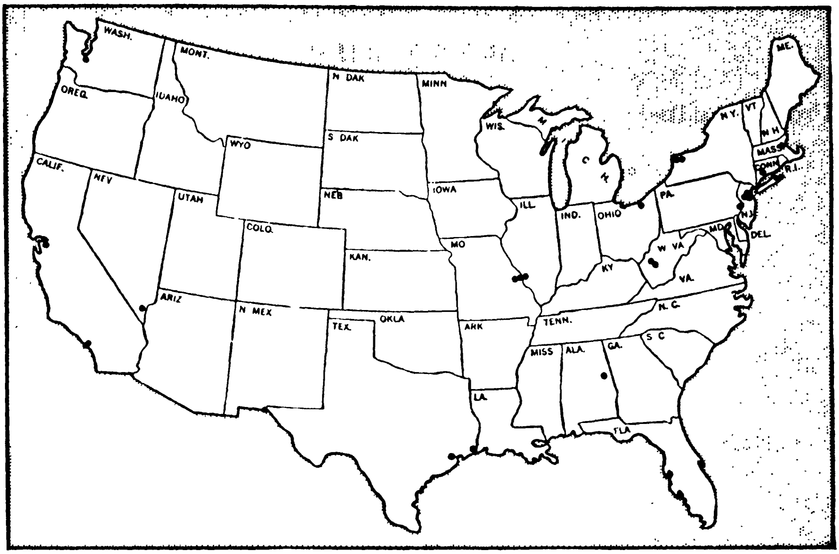
Economic Aspects

Cheap aluminum chloride was first manufactured on a large scale by a petroleum manufacturer seeking large quantities of the material for use as a catalyst in an oil-cracking process. This work led to the bauxite process described previously and a 75,000-lb-per-day (13,000-ton-per-year) plant in 1929. A single-shaft furnace 20 ft high and 5 ft in diameter produced 40,000 lb per day (about 7,000 tons per year). The smallest practical furnace of this type and hence the smallest economic plant using this process would have about one-fifth the capacity of this furnace or about 1,200 tons per year.

Plants chlorinating metallic aluminum (usually scrap) produce a much purer product and are usually somewhat smaller. Plants of this type, however, are known with capacities ranging from 500 to 12,000 tons per year. A plant of about 2,500 tons per year capacity costs about $300 per annual ton aluminum chloride. One plant of this latter size employs ten reactors.

The chief technical problem in either process is the prevention of condenser stoppage with sublimed aluminum chloride. In the bauxite furnace process, furnace maintenance is quite high because of the effect of gaseous chlorine on the brick walls.

Future production of aluminum chloride depends on its continued use in the manufacture of catalysts for synthetic rubber and in the development of various processes based on the Friedel–Crafts synthesis. The original liquid-phase oil-cracking process using aluminum chloride is employed very little any more because of newer and more efficient catalytic-cracking processes. It is quite possible that future production of aluminum chloride will be carried out largely by the petroleum refiners and synthetic-rubber manufacturers who actually use the material. It will, of course, be necessary to have a cheap source of chlorine near the manufacturing plant.



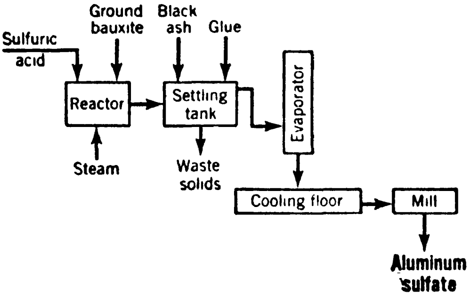
Location of Aluminum Chloride Plants

ALUMINUM SULFATE

(FILTER ALUM)

$Al_2(SO_4)_3 \cdot 18H_2O$

From Bauxite



Reaction

$$Al_2O_3 \cdot 2H_2O + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 5H_2O$$

92% yield

Material Requirements

Basis—1 ton aluminum sulfate (17% Al_2O_3)

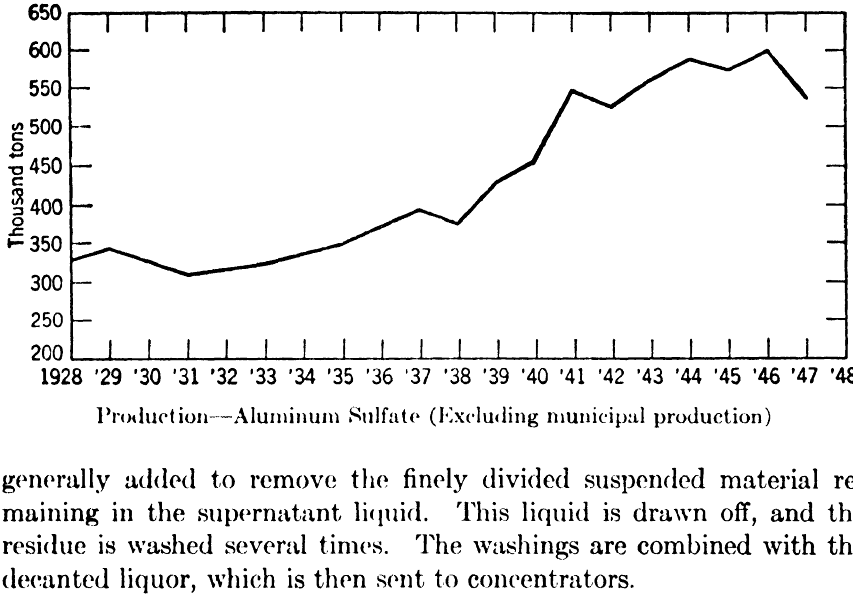
Bauxite (55% Al_2O_3)	670 lb	Black ash (70% BaS)	13 lb
Sulfuric acid (60°Bé)	1,140 lb	Flake glue	0.4 lb

Process

Aluminum sulfate is produced by the reaction of sulfuric acid on bauxite, a naturally occurring hydrated alumina ore having the approximate formula $Al_2O_3 \cdot 2H_2O$. The mined material varies in composition and generally contains 1 to 3 molecules of water plus impurities such as iron, silica, titanium, and selenium. The soluble aluminum oxide (Al_2O_3) content of a typical bauxite varies from 52 to 57 per cent and may contain 1 to 10 per cent ferric oxide (Fe_2O_3).

The crude bauxite ore is ground to a fine powder (80 per cent passes 200 mesh) and charged into open lead-lined steel reaction tanks. Sulfuric acid (60°Bé) is added, and the raw materials are thoroughly agitated, using paddle agitators, hot air, or live steam. The reaction mixture is kept at a temperature of 105 to 110°C by the live steam or lead steam coils. An excess of bauxite is fed to the reactor so that there is an excess of 0.1 to 0.2 per cent of soluble aluminum oxide. From 15 to 20 hr are required to complete the reaction. At the end of this time, a reducing material is added to the reaction mixture to reduce the iron (ferric sulfate) to a colorless ferrous condition. Barium sulfide in the form of black ash is commonly utilized, although sodium sulfide, hydrogen sulfide, sodium bisulfate, or sulfur dioxide may also be used.

If a batchwise operation is used, the charge is allowed to settle in settling tanks. Flaked glue or some similar coagulable substance is generally added to remove the finely divided suspended material remaining in the supernatant liquid. This liquid is drawn off, and the residue is washed several times. The washings are combined with the decanted liquor, which is then sent to concentrators.



Production—Aluminum Sulfate (Excluding municipal production)

The process is generally operated in a continuous manner by using a battery of combined reaction and settling tanks. A common variation of this process is the Dorr procedure, which utilizes reaction agitators in series. The reactants are thoroughly mixed and heated, using mechanical agitators, air, and live steam. Black ash (barium sulfide) is added to the last reactor to reduce the ferric sulfate. The reaction mixture is sent through a series of thickeners, operating countercurrently, which remove the undissolved material. At the same time the waste is washed thoroughly, so that it contains practically no aluminum sulfate when discarded. Glue is generally added to the first thickener as a coagulant.

The clarified aluminum sulfate solution, from the countercurrent decantation system, is concentrated in open steam-coil-heated, lead-lined evaporators. Here, the density is increased from about 35°Bé to 59 or 62°Bé. The concentrated solution is run into flat iron pans or onto a method of water treatment is a potential threat to the aluminum sulfate market.

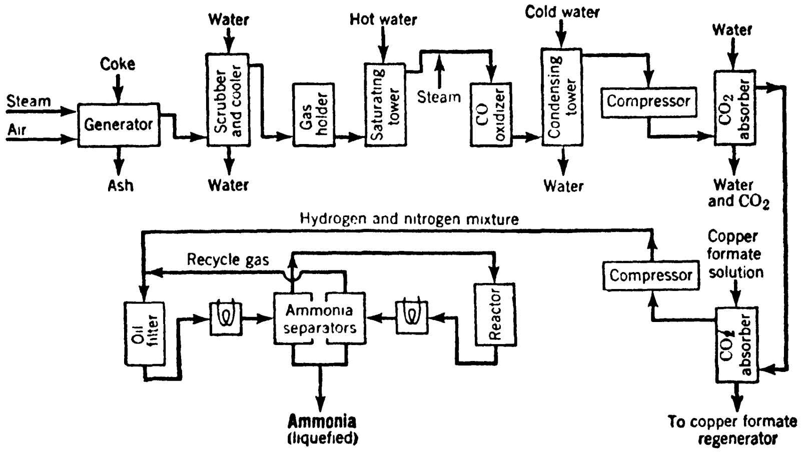
With regard to the raw material, bauxite, a continual effort is being made to replace it with cheap clays for the production of all aluminum compounds, but to date none have been economically successful. The rich bauxite deposits of the United States are practically exhausted.

One plant manufacturing a bead catalyst for catalytic cracking of petroleum makes aluminum sulfate solution (20 per cent) from purified aluminum trihydrate and sulfuric acid, in a lead-lined steel tank. A single batch contains 10 tons of aluminum sulfate on the dry basis.

AMMONIA

NH_3

By Catalytic Synthesis from Nitrogen and Hydrogen



Reaction

$$N_2 + 3H_2 \rightarrow 2NH_3$$

85% yield

Heat and Material Requirements

Basis—1 ton ammonia (liquefied)

Coke	1.78 ton
Water	31,000 gal
Coal (steam and power)	2.3 ton

Process

Nitrogen and hydrogen in a 1-to-3 ratio react catalytically at high temperatures and pressures to produce ammonia. The nitrogen is derived from the air by means of liquefaction, the producer gas reaction, or by burning out the oxygen in air with hydrogen. Hydrogen is obtained from many sources, such as water gas or natural gas, or by the electrolysis of water or brine. See *Hydrogen* for other sources and details.

The basic process for synthetic ammonia is the Haber-Bosch system. Many other processes have been proposed and used, but these may be considered as variants of the original method. The American system (Nitrogen Engineering Corporation), a modified Haber-Bosch method, is pictured on the flowsheet and operates approximately as follows:

Water gas (blue gas) is produced by passing steam through incandescent coke at a temperature of 1,000°C or higher. The reaction $C\ (\text{amorph}) + H_2O \rightarrow CO + H_2$ yields almost equal amounts of carbon monoxide (about 44 per cent) and hydrogen (47 per cent), plus small amounts of carbon dioxide (4 per cent) and nitrogen (4 per cent). The source of nitrogen is producer gas which is made by passing air and steam through incandescent coke. This is an exothermic reaction and may be run alternately with the endothermic water–gas reaction to reheat the coke. If the latter is done, the gas is called "blow gas." Nitrogen (about 54 per cent), carbon monoxide (30 per cent), hydrogen (10 per cent), and carbon dioxide (4 per cent) are the chief constituents of producer gas.

The water gas and the producer gas (or "blow gas"), after scrubbing and cooling with water, are properly adjusted to the desired ratio (3-to-1 hydrogen–nitrogen) and are saturated with water vapor in a hot-water scrubber. After the gases are treated with steam and heated further in exchangers, they are passed over an iron oxide catalyst to convert the carbon monoxide to carbon dioxide according to the following equation: $CO + H_2O \rightarrow CO_2 + H_2$. The carbon dioxide is removed by cooling the gases and compressing them to about 25 atm and washing with water at this pressure. About 50 per cent of the energy required for compression is recovered in a water-turbine system.

The gas mixture of 3 parts of hydrogen and 1 part of nitrogen, containing about 2 per cent carbon monoxide, is compressed with cooling to 200 atm. The carbon monoxide and any small amounts of oxygen are removed by washing with a solution of ammoniacal cuprous formate which is regenerated and re-used.

The purified 3-to-1 hydrogen–nitrogen mixture is raised to the full compression of 300 atm and is mixed with the recompressed, recirculated gases. After passing through an oil filter and a water–ammonia cooler–condenser to remove residual ammonia, the gases are raised to 475°C in heat exchangers and are passed through the reactor.

The reactor contains an iron oxide catalyst which has been promoted by addition of small amounts of aluminum oxide (3 per cent) and potassium oxide (1 per cent by weight based on the iron oxide). The catalyst is prepared by burning iron to the oxide, fusing it, and dissolving the promotors in the molten material. The mass is cooled and crushed to the desired particle size and is strong enough to be packed in the catalyst tubes *per se.* The iron oxide is reduced to iron in the catalyst chamber by the nitrogen–hydrogen mixture, leaving a porous iron containing the various promoter materials. The catalyst is ruined by contact with phosphorus, arsenic, and sulfur; carbon monoxide greatly reduces its activity.

The gases leaving the reactor are cooled (−10 to −20°C), and some of the ammonia liquefies. Part of the gas is purged to prevent accumulation of diluents such as argon, and the purge gas is used for fuel. The remaining gas is recompressed and recycled. The conversion per pass is approximately 20 to 22 per cent and the over-all yield with recirculation approaches 85 to 90 per cent.

The salient features of the other systems in operation are:

✓***Haber-Bosch.*** Low-pressure system operating at 200 atm and 550°C. Uses a promoted iron oxide catalyst and realizes a 5 to 10 per cent conversion per pass. The reactor exit gas is recycled.

Claude. Very high-pressure system operating on a promoted iron catalyst at 500 to 650°C and 900 to 1,000 atm. The gas is not recycled. Instead, it is passed through a series of converters. The conversion for a single converter is about 40 per cent, and a yield of 85 per cent is realized after passage through the converter series.

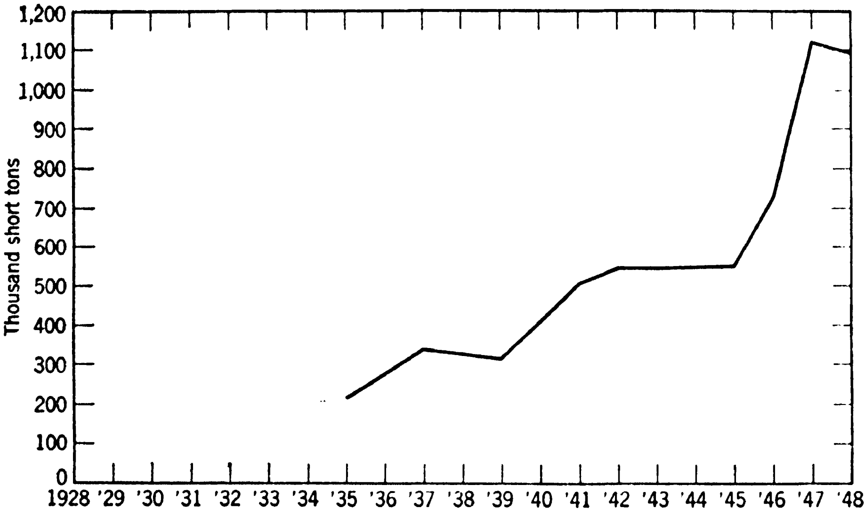
Casale. Promoted iron catalyst at 500°C and 600 atm pressure. Recirculates reactor exit gas and has a 15 to 18 per cent conversion per pass.

Fauser. Operates at 200 atm, using electrolytic hydrogen generated by a special cell (Fauser cell). Other conditions are the same as for the Casale system; a 12 to 23 per cent conversion per pass is realized.

Mont Cenis. Lowest-pressure system, operating at 100 atm on an iron cyanide complex catalyst at 400 to 425°C. The conversion per pass (reactor exit gas is recycled) is 9 to 20 per cent.

du Pont. A modified Claude Casale system operating on coke which alternately produces "blue gas" (water gas) and "blow-run gas" as raw materials. Residual carbon monoxide is hydrogenated to methane and is used as a diluent instead of being absorbed with ammoniacal cuprous formate. The carbon dioxide is removed by washing with water under 30 atm pressure. About 60 per cent of the energy expended is recovered in the so-called "mountain recovery" system, in which the pressure of the water forces it to the top of a mountain where the carbon dioxide escapes and the denuded water flows down again to the pumps possessing nearly 300 lb actual pressure. This procedure eliminates water purification since the water may be re-used. The system uses a series of metal converters (Claude process) but also recycles some of the residual gas.

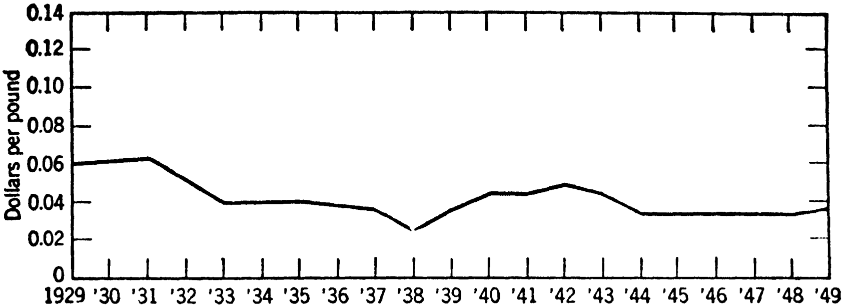
Natural Gas (Mathieson). Natural gas is preheated, passed over a bauxite catalyst to remove the sulfur, and then treated with steam in alloy-steel tubes at 30 psi and 1,300°F. More steam, methane, and air are added, and the methane and carbon monoxide are burned at 2,000°F in a combustion chamber yielding hydrogen (40 per cent), carbon monoxide (11 per cent), carbon dioxide (4 per cent), and water (28 per cent). The gas is quenched to 800°F, and an iron catalyst plus steam reduces the carbon monoxide to below 1 per cent. The gas is cooled, stored, compressed to 200 psi, cooled to 100°F; the carbon dioxide absorbed by monoethanolamine solution; the gas compressed to 2,100 psi; and the residual carbon monoxide removed by cuprous and cupric formate. The synthesis takes place at 4,000 psi and 925°F (495°C) on promoted iron; the gas leaving at 375°F contains 16 per cent ammonia.



Production—Ammonia (Synthetic, anhydrous, private plants only)

Use Pattern

	1947 (est.), per cent
Fertilizer	45
Industrial	33
Ordnance (foreign)	22
	100



Price—Ammonia, Anhydrous

Miscellaneous

Properties. Anhydrous ammonia is a colorless gas with a characteristic pungent odor.

Mol. wt.	17.03	M.P.	−77.7°C
Sp. gr.	0.817 (−79°C)	B.P.	−33.4°C

Density (air = 1) 0.5971

Very soluble in water; one volume of water dissolves 700 volumes of ammonia at 20°C. Soluble in alcohol and ether at room temperature. At about 1,290°F or in the presence of an electric spark, anhydrous ammonia is dissociated into nitrogen and hydrogen. Anhydrous ammonia is readily liquefiable at moderate pressures and temperatures and is commonly referred to as liquid ammonia. At room temperature a pressure of about 175 psi is required to keep the ammonia gas in a liquid state.

Grades. Anhydrous: pure or refrigeration grade containing 99.95 per cent NH_3 minimum; technical, commercial, or fertilizer grade containing 99.5 per cent NH_3 minimum.

Aqua: C.P. and USP containing about 28 per cent NH_3. Technical containing about 29.4 per cent (26°Bé) NH_3. Also 16, 18, and 20°Bé solutions. Aqua ammonia is a water solution of ammonia and is also referred to as ammonia water or liquor and ammonium hydroxide or hydrate.

Containers and Regulations. Anhydrous ammonia is shipped in the liquid state in pressurized steel tank cars, bottle-type steel cylinders, and tube-type steel cylinders. It is classified as a nonflammable compressed gas and requires a green ICC shipping label. Aqua ammonia is shipped in steel tank cars, trucks, drums, glass carboys, and bottles.

Economic Aspects

Before World War I, the world's primary supply of fixed nitrogen was Chili saltpeter. With the advent of the Haber process for the pressure synthesis of ammonia from nitrogen and hydrogen, the situation changed in favor of synthetic ammonia. During the early years of the synthetic process, some competition on a world scale came from the arc process (Birkland-Eyde) and the cyanamid process. However, all synthetic ammonia produced in the United States is made by pressure synthesis. The well-known cyanamid plant at Niagara Falls, Ontario, still operates but is a minor factor in American ammonia supply. During the last war the Germans developed a continuous rotary furnace which supposedly offered economic advantages over the conventional cyanamid process.

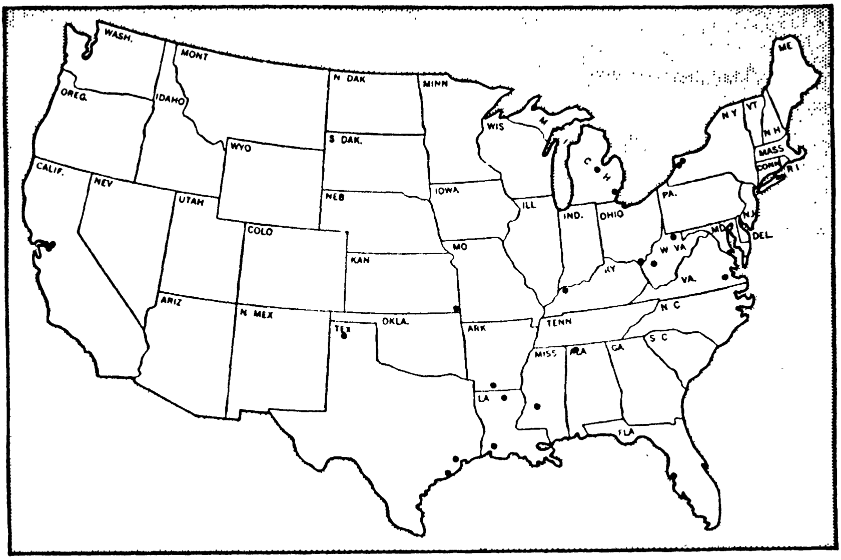
Competition among various synthetic processes centers around hydrogen preparation and purification, type of catalyst, and synthesis pressure. The most economic process depends on many factors, not the least of which is the patent situation. The chief change in the synthetic-ammonia process during the recent war was in the source of hydrogen. Prior to the war almost all synthetic-ammonia hydrogen was produced from coke or coal; at present about 40 per cent of production is from natural gas. Synthetic-ammonia production is a tonnage industry, and some of the plants are so designed that they may readily be converted to methanol production, if feasible.

The smallest economic unit has been determined by one company to have a daily production of 300 tons (100,000 tons per year). Plant sizes vary, however, from less than 5,000 tons to over 200,000 tons per year. Ordnance plants built during the war were generally in units of 50,000 tons annual nitrogen capacity, with 1 to 3 units in each plant. The commonly accepted figure for capital costs is $150 per annual ton of ammonia. In contrast, the cyanamid plant at Niagara Falls has a capacity of 355,000 tons per year (which is equivalent to 75,000 tons fixed nitrogen per year). The capital cost for such a plant is estimated as $600 per ton fixed nitrogen per year.

A minor amount (25 per cent of the total ammonia production in 1939, 16 per cent in 1944) of impure ammonia is recovered from coke-oven gases but is usually converted into ammonium sulfate. Very little is sold as ammonia (6 per cent).

The future of the fixed-nitrogen industry just after the war was complicated by the presence of Government-owned plants, extra capacity in Canada, and increased by-product coke-oven capacity. During the peak year of the war almost 75 per cent of the anhydrous ammonia available went for military use, but instead of a sharp decrease in ammonia requirements after the war production continued to climb, largely because of foreign and domestic requirements for ammonium nitrate and the development of direct ammonia addition to soils. The annual consumption of ammonia in fertilizers in the last two years is at least 2.5 times the prewar rate and is still increasing.

The accompanying map of geographical plant distribution includes both private and Government-owned synthetic-ammonia plants. By-product coke-oven facilities are shown under *Ammonium Sulfate.*

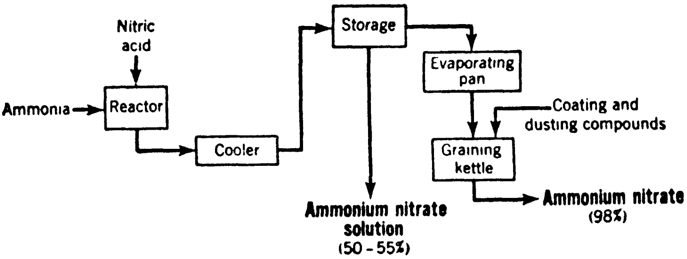


Location of Synthetic-Ammonia Plants

AMMONIUM NITRATE

NH_4NO_3

From Ammonia and Nitric Acid



Reaction

$$NH_3 + HNO_3 \rightarrow NH_4NO_3$$

99% yield

Material Requirements

Basis—1 ton ammonium nitrate (98%)

Ammonia	440 lb
Nitric acid	1,630 lb

Process

Ammonium nitrate is formed in solution by reacting ammonia and nitric acid. The solution is evaporated, crystallized, and dried to give the commercial product.

Gaseous ammonia is introduced into a stainless-steel reactor or saturator beneath the surface of an aqueous ammonium nitrate solution. Simultaneously, nitric acid, usually of 40 per cent concentration, is fed into the reactor at a rate to give equimolar concentrations of the two reactants. As the materials come into contact, the heat of reaction causes the solution to boil, thus concentrating it partially.

The reaction is usually run continuously by taking off an aqueous solution varying in strength from 45 to 68 per cent ammonium nitrate.

After passing through cooling coils, the nitrate solution is stored for further processing or for shipment in solution form. This water solution, known as ANW, is usually shipped as a 50 to 55 per cent solution or as high as 75 per cent ammonium nitrate. The latter is difficult to unload because of the solid salt deposit which forms in cold weather, thereby necessitating a steaming operation for removal.

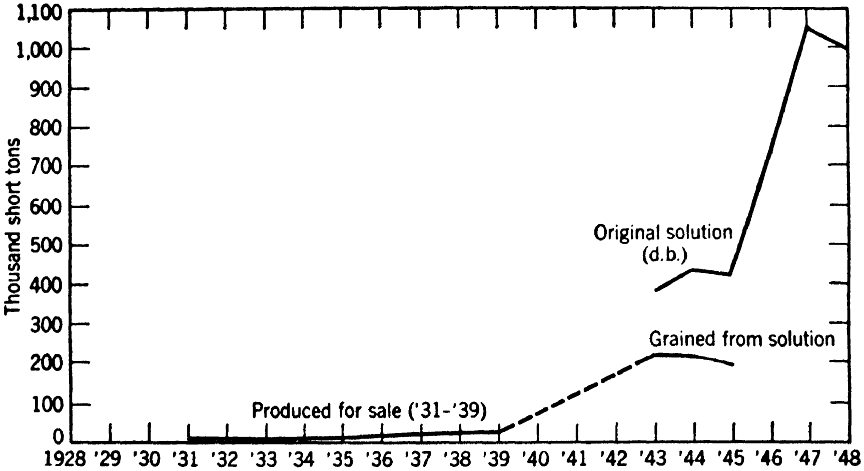
For the production of solid ammonium nitrate, three general methods are used. These are designed to overcome the undesirable caking tendencies of ammonium nitrate, caused by adsorption of moisture from humid air. By producing coarse granules of salt having desirable physical properties and by conditioning the particles with a water-repellent film and dusting, the humidant properties of the salt are reduced. This enables the manufacture of a product suitable for fertilizer mixes as well as for dynamite compositions.

In the batch-graining process, the aqueous solution of ammonium nitrate is gravity-fed from the storage tank to open pans (high pans) fitted with stainless-steel or aluminum heating coils. While using air agitation, the solution is evaporated to about 2 per cent water content at a maximum temperature of 320°F. The 98 to 98.5 per cent ammonium nitrate solution then flows through pipes into a special flat graining kettle. Here it is stirred by slowly revolving stainless-steel paddles until the crystallized nitrate is dried to about 0.1 per cent moisture. Under this rolling motion, rounded grains of minimum surface are secured. Grain size is controlled by temperature and rate of precipitation and may be varied greatly, depending on the end use. When the granulation reaches a certain point, about 0.3 per cent of a coating compound, for example, mixtures of rosin and paraffin, and about 1 per cent of a dusting agent (kieselguhr, clay, or calcium carbonate) are added to yield a free-flowing ammonium nitrate which is water-resistant and noncaking. This material is suitable for use in dynamite but is usually not water-resistant enough for fertilizer use.

The second method, a continuous process known as spray granulating, "prilling," concentrates the aqueous solution from the reactor to about 95 per cent ammonium nitrate. The hot (280 to 285°F) solution of nitrate is then pumped from the evaporator to the top of a spraying tower (20 ft square by 70 ft high), whence it is discharged through a spray head. As it falls, the solution crystallizes into small, spherical particles (called "prills") about the size of buckshot. The particles are dried further and dusted with a compound such as fine diatomaceous earth to minimize caking tendencies. Because the "prilled" material is freer from fines and coarser than grained ammonium nitrate, it requires less conditioning to give a product suitable for fertilizers. From this process, an ammonium nitrate is produced and marketed as "Nitraprill" fertilizer. It analyzes 33.5 per cent nitrogen and is packed in double asphalt-laminated paper bags with waxed sewn ends to protect the product in storage under all weather conditions.

A third process for making solid ammonium nitrate is continuous vacuum crystallization. The ammonium nitrate solution (about 60 per cent) formed in the reactor is concentrated by evaporation (*ca.* 150°F) to between 75 and 80 per cent dry substance. It is then charged into a special polished stainless-steel vacuum crystallizer, somewhat similar to the Oslo-Krystal classifying type used for ammonium sulfate, but modified to give a rotating rather than a classified suspension and to provide adequate growth of seed crystals to intermediate sizes. By operation at a temperature of about 97°F, an absolute pressure of 25 mm Hg, and a concentration of 75 to 79 per cent ammonium nitrate, crystals of size, shape, and strength favorable for fertilizer use are produced continuously at a relatively high rate.

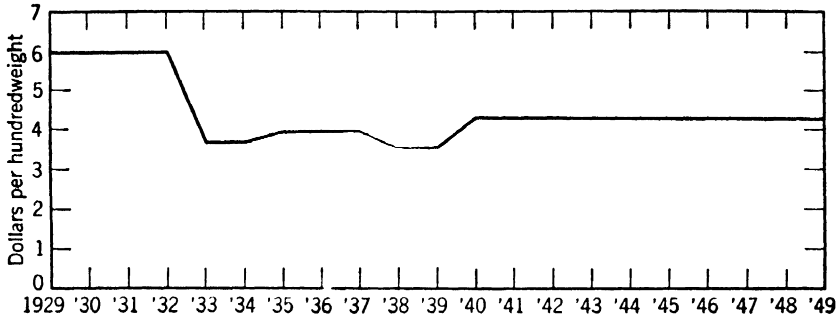
The product is removed from the bottom of the crystallizer in a slurry containing about 40 per cent by weight of crystals and run to a centrifuge. The mother liquor is returned to the system, while the crystals, containing about 1 per cent water, are fed to a counterflow rotary dryer, where at 180°F the moisture content is reduced to about 0.1 per cent. The crystals are usually conditioned by dusting (3 to 4 per cent kieselguhr, for example) and then packaged in bags.



Production—Ammonium Nitrate (100% NH_4NO_3—not including military production during World War II)

Use Pattern

	1948 (est.), per cent
Fertilizer	80
Explosives and other industrial	20
	100



Price—Ammonium Nitrate

Miscellaneous

Properties. White hygroscopic crystals, which are relatively unstable, forming explosive mixtures with combustible materials or when contaminated with certain organic compounds.

Mol. wt.	80.05	M.P.	169.6°C
Sp. gr. (α)	1.66 25°/4	B.P.	Slowly decomposes 210°C
	Nitrogen content	35%	

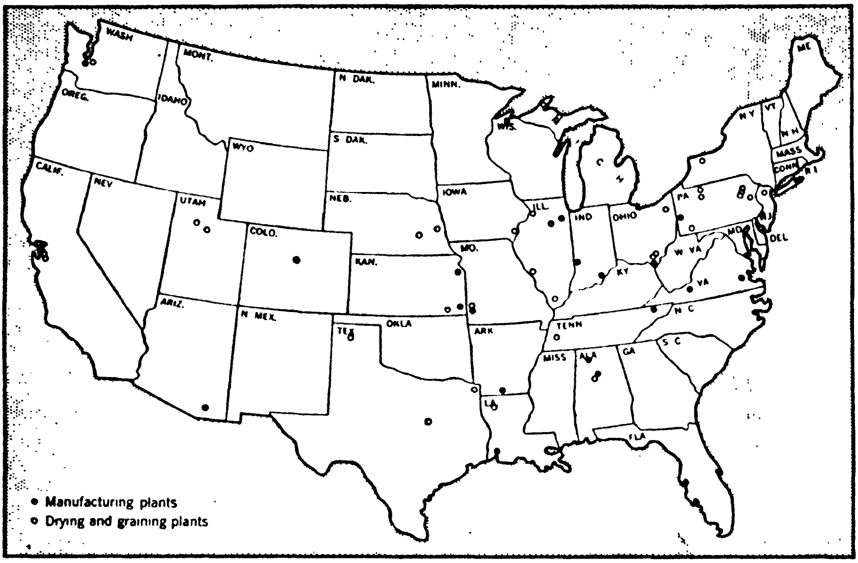
Ammonium nitrate may exist in 5 or 6 crystalline forms, depending on the temperature and pressure. Very soluble in water (55 per cent at 0°C, 90 per cent at 100°C), alcohol (3.7 per cent at 20°C), methyl alcohol (14.6 per cent at 20°C), and ammonia.

Grades. C.P. (crystalline and granular), technical (granular—98 to 100 per cent), and fertilizer or conditioned (93 to 96 per cent containing 32.5 to 33.5 per cent nitrogen).

Containers and Regulations. Bags or bulk in tight lined cars, casks, barrels, drums, kegs, asphalt-lined paper bags, boxes, and bottles. Yellow ICC shipping label required. Classified as an explosive ingredient, and its manufacture, use, storage, distribution, and possession are regulated by the Federal Explosives Act, administered by the Bureau of Mines.

Economic Aspects

The chief use of ammonium nitrate in the past has been in the explosives industry as a constituent of dynamite and amatol (a mixture of ammonium nitrate and TNT). Its use in fertilizer was limited because of its hygroscopic properties and consequent tendency to set in large blocks (so-called "tombstones") instead of remaining in a free-flowing granular form that could be applied to the soil in agricultural drills.



Location of Ammonium Nitrate Plants

This difficulty has been partially solved by coating the granules with kieselguhr or a mixture of petrolatum, paraffin, and rosin. This is costly, and various processes have been studied to produce crystals of such shape, size, and form that simpler and cheaper coatings may be used. It is also imperative that graining be carefully controlled to avoid localized high temperatures and contamination with organic substances, since the industry has a long record of serious explosions in high-pan grainers.

For economy, plant size should vary in annual capacity from 50,000 to 200,000 tons. A high-pan graining plant in this size range costs approximately $10 per annual ton capacity. The plant cost of the more recently proposed processes, for example Krystal, prill, and continuous graining, are said to be 65 to 85 per cent of the high-pan investment.

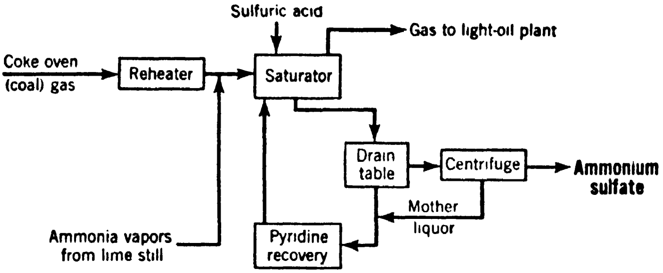
As a fertilizer material, ammonium nitrate competes with sodium nitrate and ammonium sulfate, which have been dominant in the top and side dressing of crops. In the fertilizer field as a whole, ammonium compounds have made great strides during the past 20 years at the expense of natural organic compounds. Twenty years ago, 25 per cent of U. S. fertilizer nitrogen came from natural organics; present utilization is about 5 per cent. Many Ordnance plants that would normally have been shut down after the war were put back into operation (as far as ammonium nitrate facilities were concerned) either by private owners, who have purchased a few of the plants, or by lessees in those plants still owned by the Government.

In 1947, ammonium nitrate accounted for about 20 per cent of the domestic nitrogen production for plant nutrients. Normally, this figure might have been expected to be on the increase, but the disastrous explosions at Texas City and Brest in 1947 will undoubtedly curtail ammonium nitrate fertilizer use for a while. One check on increased use of ammonium nitrate as a fertilizer, however, is increased direct use of both anhydrous and aqua ammonia, which in many cases is more economical than ammonium nitrate use.

AMMONIUM SULFATE

$(NH_4)_2SO_4$

From Coal Gas



Yield

23 lb per ton of coal

95–97% recovery

Process

Ammonium sulfate is produced in by-product coking plants by the reaction of ammonia in the coal gas with sulfuric acid. In the usual high-temperature coking process, approximately 15 to 20 per cent of the nitrogen of the coal appears in the crude coal gas as ammonia. This gas, on leaving the by-product coke oven, contains on the average about 0.5 lb ammonia per 1,000 cu ft gas (1.1 per cent by volume) corresponding to 5.5 lb ammonia per ton of coal.

The recovery of ammonia, as well as the purification of the coal gas, may be accomplished by using one of several methods. In general, there are three methods of ammonia recovery, although there are several modifications of each. These methods are similar in several aspects; that is, in most cases the hot gases from the ovens are precooled in the collecting mains, and eventually the gases are passed through an acid bath (saturator). For a general treatment of coal gases, see *Coke*.

The oldest ammonia-recovery process, called the indirect method, takes the precooled vapors from the collecting main and cools them further in indirect tubular coolers with the aid of water. Tar and ammonia-water separate, and the gases, after having been freed from fog by tar separators, are washed countercurrently with weak ammonia liquor and water. The scrubbed gases then pass to the light-oil plant. The various ammonia liquors are collected, separated from the tar, and distilled with steam. A slurry of lime is added to the still to decompose the fixed ammonium salts (such as ammonium chloride). The gases leaving the top of the still contain mostly ammonia (plus some pyridine) and are passed through a saturator containing sulfuric acid.

The direct method involves passing the gases from the foul main, directly into a saturator without preliminary tar separation. The method was designed to eliminate ammonia absorption by water. However, tar of inferior quality separates, the ammonium sulfate is badly contaminated with tar, and, finally, the sulfuric acid decomposes the ammonium chloride, liberating hydrogen chloride, which severely attacks the equipment.

The third method, a compromise between the previous two, is called the semidirect process.

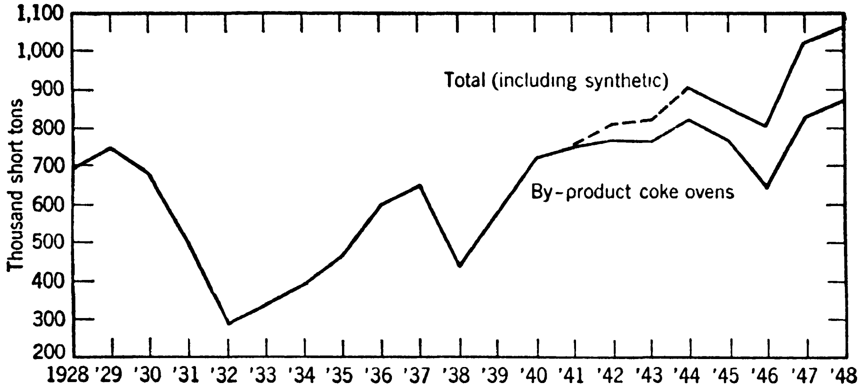
Coke-oven gases are precooled in the collecting main and then passed through condensers where they are cooled further (about 32°C) to a point at which substantial quantities of water as well as most of the tar separate (see *Coke*). The water, which contains a major part of the fixed ammonium salts plus a small percentage of dissolved free ammonia, is collected and distilled in a lime still. See *Ammonia* for details. The ammonia evolved may be added to the main gas stream after it has been freed of tar fog in the final tar extractor. The gases leaving the final tar separator (before ammonia addition from the lime still) contain about 75 per cent of the ammonia originally present. These gases are heated above their dew point by passage through a reheater (60 to 70°C) and are then bubbled beneath the surface of a 5 to 10 per cent sulfuric-acid solution contained in an enclosed lead-lined steel saturator. Make-up sulfuric acid (60°Bé) is added at intervals to retain the desired acid concentration. A reaction temperature of 50 to 60°C is maintained by both the gas reheater and the exothermic neutralization reaction.

Crystals of ammonium sulfate settle to the bottom of the continuous saturator whence they are discharged onto a draining table. The mother liquor is either processed for pyridine recovery (see *Pyridine*) or returned directly to the saturator. The drained crystals are charged into either a batch or a continuous centrifuge, where a short water wash is generally employed to reduce acidity to a minimum. The dried ammonium sulfate is discharged from the centrifuge and bagged. The yield of ammonium sulfate per ton of coal containing between 1 and 1.5 per cent nitrogen averages about 23 lb.

The gas leaving the saturator at 45 to 60°C is cooled and passed to the light oil-recovery plant. See *Coke* and *Benzene* for details.

From Synthetic Ammonia and Sulfuric Acid

Relatively small quantities of ammonium sulfate are manufactured by the reaction of synthetic ammonia and concentrated sulfuric acid. The process produces a very pure product which has a limited demand. Large quantities have been produced by this method in the past only during emergencies or shortages.



Production—Ammonium Sulfate

The process is essentially the same as the one described previously, using coal gas as one of the raw materials. The actual process details vary among different manufacturers.

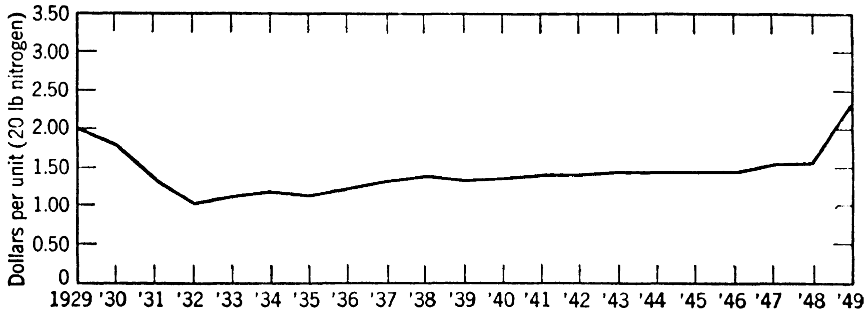
One plant produces a high-grade ammonium sulfate as follows: Anhydrous ammonia is dissolved in water and pumped as an 18 to 26 per cent solution to a reactor where it meets a stream of sulfuric acid. The solution of ammonium sulfate (maintained at 3.5 *p*H) that forms is pumped into double-effect crystallizers. Here the water is evaporated under vacuum, leaving a metastable, supersaturated solution, which readily crystallizes. The crystals grow in size until they are heavy enough to settle to the bottom of the crystallizer. A slurry, containing 55 to 60 per cent by volume of crystals, is discharged into automatic centrifuges. The crystals are spun dry, rinsed with water, and discharged onto a belt conveyer, which carries the product to storage hoppers. The ammonium sulfate crystals, obtained in practically theoretical yield, are packaged in multiwall paper bags. The mother liquor from the centrifuges is returned to the crystallizers.

Ammonium sulfate may also be produced, using gypsum instead of sulfuric acid, according to the following reactions: $2NH_3 + CO_2 + H_2O$

$\rightarrow (NH_4)_2CO_3$; $(NH_4)_2CO_3 + CaSO_4 \cdot 2H_2O \rightarrow (NH_4)_2SO_4 + CaCO_3 + 2H_2O$. Finely ground gypsum ($CaSO_4 \cdot 2H_2O$) or anhydrite ($CaSO_4$) is suspended by agitation in about twice its weight of water. Ammonia and carbon dioxide are passed into the mixture, forming ammonium carbonate, which then reacts with the calcium sulfate (gypsum), forming calcium carbonate and ammonium sulfate, the latter dissolving in the water. At the end of the reaction (6 to 9 hr), the 25 per cent ammonium sulfate solution is filtered to remove the insoluble calcium carbonate. The clear solution is concentrated in evaporators to crystallize out the ammonium sulfate. The crystals are centrifuged and may be further dried in a rotary dryer; the mother liquor is returned to the reactor for subsequent batches.

Use Pattern

	Per cent
Fertilizer	97
Industrial (water treatment, fermentation, fireproofing, tanning)	3
	100



Price—Ammonium Sulfate

Miscellaneous

Properties. White to brownish gray crystals.

Mol. wt.	132.14	M.P.	513°C with decomposition
Sp. gr.	1.769 20°C/4		

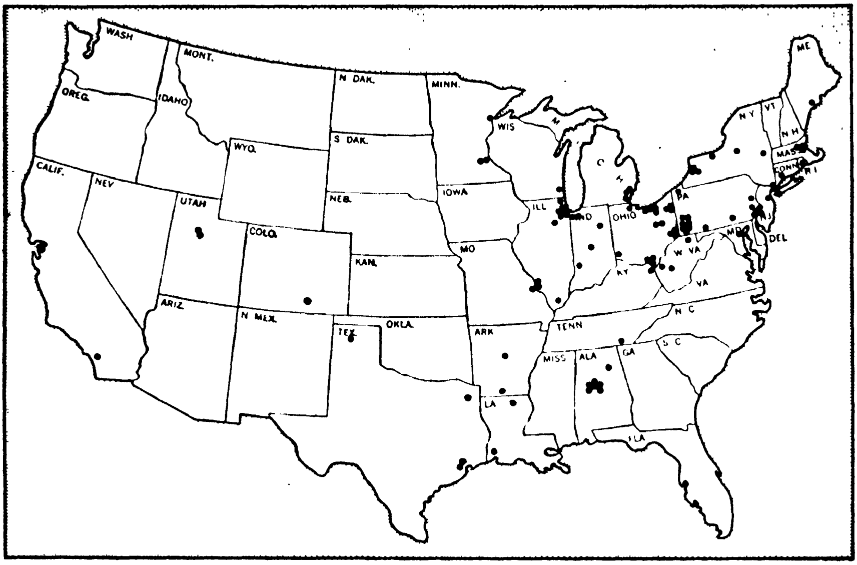
Soluble in water (70.6 g per 100 ml at 0°C, 103.8 g per 100 ml at 100°C), very slightly soluble in alcohol. Insoluble in acetone.

Grades. Commercial, technical, and C.P.

Containers and Regulations. Barrels, bags, kegs, boxes, and bottles. No ICC shipping label required.

Economic Aspects

Most ammonium sulfate is produced by the by-product coke industry by reacting the primary by-product, ammonia liquor, with sulfuric acid. The product need not be highly purified, since its major use is as fertilizer. This fact allows coke-oven operators to dispose of impure ammonia liquors for which there is little demand because of cheap pure synthetic ammonia. Actually, there is some doubt as to the economics of recovering ammonia from coke-oven gases. However, if the gases are to be used as fuel, ammonia removal is necessary. A method of preventing ammonia formation during the coking of coal would be very useful to the industry.



Location of Ammonium Sulfate Plants

Of the three methods in common use for ammonia recovery as ammonium sulfate the direct method is not suitable where tar must be removed first in a separator; the semidirect method uses much less steam and water than the indirect process and requires a lower capital investment.

For economy's sake, the by-product recovery plant usually serves several batteries of coke ovens. The smallest economic unit is generally considered two batteries of 59 ovens each. Some gas units may have as few as 10 ovens in a battery, in which case ammonia liquor will be sold to a central plant for conversion to ammonium sulfate. The yield per ton of coal carbonized depends on the quality of the coal; a figure of

23.5 lb ammonium sulfate per ton of coal carbonized may be expected from 11,300 Btu coal. The industry's average yield since 1920 has varied from 20 to 25 lb.

In 1948, there were 86 operating by-product coke-oven installations in the United States, of which 81 recovered ammonia in one form or another. Actually, 64 produced ammonium sulfate, and 21 produced ammonia liquor. The apparent discrepancy in the figures results from duplication in that 4 plants produced both ammonium sulfate and ammonia.

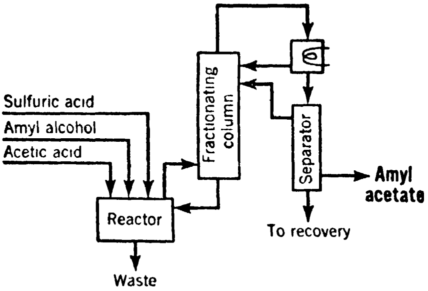
The recent agricultural nitrogen shortage has led to the installation of several plants making ammonium sulfate from synthetic ammonia and sulfuric acid. Several chemical companies have made comparatively small amounts of a pure product by this method for many years. A few coke-oven operators are adding synthetic ammonia to the tar-free coke oven gases in order to operate recovery facilities at maximum capacity.

The average by-product ammonium sulfate installation produced 8,000 tons in 1946, although individual plant capacities were both much smaller and much larger. Recovery facilities for such an average size plant probably cost about $15 to $20 per annual ton capacity.

AMYL ACETATE

$CH_3COOC_5H_{11}$

From Amyl Alcohol and Acetic Acid by Esterification



Reaction

$$C_5H_{11}OH + CH_3COOH \xrightarrow{H_2SO_4} CH_3COOC_5H_{11} + H_2O$$

90% yield

Material Requirements

Basis—1 ton amyl acetate

Amyl alcohol (normal)	1,600 lb
Acetic acid (glacial)	1,025 lb
Sulfuric acid (66°Bé)	2 to 8 lb

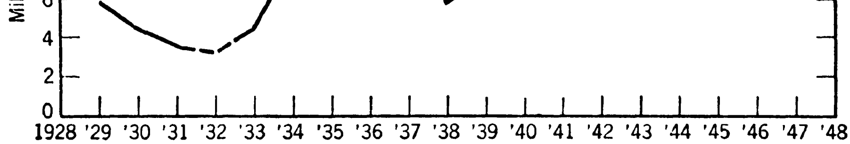
Process

Amyl acetate is produced by the esterification of acetic acid with amyl alcohol in the presence of catalytic quantities of sulfuric acid. The esterification process is theoretically identical with the one used for butyl acetate. See *Butyl Acetate* for details. Certain modifications must be made, depending on the type of alcohol used. The primary amyl alcohols react more readily than the secondary and tertiary alcohols. The yields of esters vary and are roughly proportional to the alcohol reactivity.

Generally, amyl acetate is produced batchwise. Glacial acetic acid, *n*-amyl alcohol (10 per cent excess), and 0.1 per cent sulfuric acid (66°Bé) are refluxed in a still until equilibrium is attained. At a column-head temperature of about 95°C a ternary azeotrope (10.5 per cent ester, 33.3 per cent alcohol, and 56.2 per cent water, B.P. 94.8°C) is collected and separated in a continuous separator. When all the water of reaction and most of the alcohol have been removed, *n*-amyl acetate is distilled and sent to storage. The yield of the ester based on the acetic acid charged is about 90 per cent. The purity of amyl acetate depends on the raw materials used, as well as the sharpness of the fractionation. Commercial amyl acetate assays 85 to 88 per cent ester, whereas pure amyl acetate contains 95 to 99 per cent ester.

Fusel oil, a by-product obtained in the manufacture of ethyl alcohol by fermentation, is a naturally occurring blend of alcohols. The chief components of this oil are isoamyl and normal amyl alcohol. Since refined fusel oil (about 85 per cent isoamyl alcohol) finds extensive use in the production of amyl acetate, the commercial grades of the latter contain more of the isoamyl ester than the normal amyl ester.

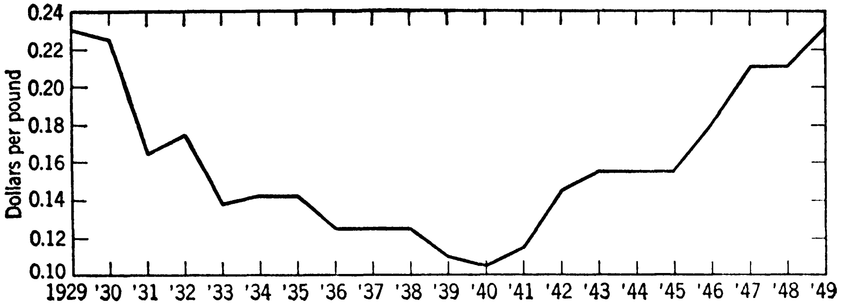
The other acetates of amyl alcohol may be prepared by the same process (with modifications), using the corresponding alcohol. Normal amyl acetate, isoamyl acetate (as well as mixtures thereof), and secondary amyl acetate are the most important commercially.



Production—Amyl Acetate (*n*-, *sec*-, *iso*-, 90%)

Use Pattern

	1947 (est.), per cent
Lacquer solvent	70
Penicillin recovery	25
Miscellaneous	5
	100



Price—Amyl Acetate (From pentane since 1933)

Miscellaneous

Properties. *n-Amyl acetate* ($CH_3COOCH_2CH_2CH_2CH_2CH_3$). Colorless liquid with a pear- or banana-like odor.

Mol. wt.	130.18	M.P.	−70.8°C
Sp. gr.	0.879 20°C/20	B.P.	148.4°C (737 mm)
	Weight per gallon	7.22 lb (20°C)	

Soluble in alcohol and ether in all proportions at room temperature. Very slightly soluble in water.

Flash point (closed cup)	77°F
Ignition temperature	750°F
Vapor density (air = 1)	4.49
Explosive limits (% by volume in air)	Lower 1.1

Isoamyl acetate [$CH_3COOCH_2CH_2CH(CH_3)_2$]. Colorless liquid with a banana-like odor.

Mol. wt.	130.18	M.P.	−78.5°C
Sp. gr.	0.876 15°C/4	B.P.	142°C (757 mm)
	Weight per gallon	7.30 lb (15°C)	

Soluble in alcohol and ether. Very slightly soluble in water (0.25 per cent) at 15°C.

Flash point (closed cup)	92°F
Ignition temperature	715°F
Vapor density (air = 1)	4.49

sec-Amyl acetate [$CH_3COO\ CH(CH_3)CH_2CH_2CH_3$]. Colorless liquid.

Mol. wt.	130.18		
Sp. gr.	0.876 15°C/4	B.P.	142°C (757 mm)
	Weight per gallon	7.30 lb (15°C)	

Soluble in alcohol and ether in all proportions at room temperature. Slightly soluble in water (0.25 g per 100 ml at 15°C).

Flash point (closed cup) 89°F

Active amyl acetate [$CH_3COOCH_2CH(CH_3)CH_2CH_3$]. Colorless liquid.

Mol. wt.	130.18		
Sp. gr.	0.880 (12.5°C)	B.P.	141 to 142°C

Soluble in alcohol and ether. Very slightly soluble in water.

sec-Amyl acetate or *diethylcarbinol acetate* [$CH_3COOCH(CH_2CH_3)_2$]. Colorless liquid.

Mol. wt.	130.18		
Sp. gr.	0.871 20°C/4	B.P.	131°C

Soluble in alcohol and ether. Slightly soluble in water.

tert-Amyl acetate [$CH_3COOC(CH_3)_2CH_2CH_3$]. Colorless liquid.

Mol. wt.	130.18		
Sp. gr.	0.874 (19°C)	B.P.	124.5°C (740 mm)

Soluble in alcohol and ether. Very slightly soluble in water.

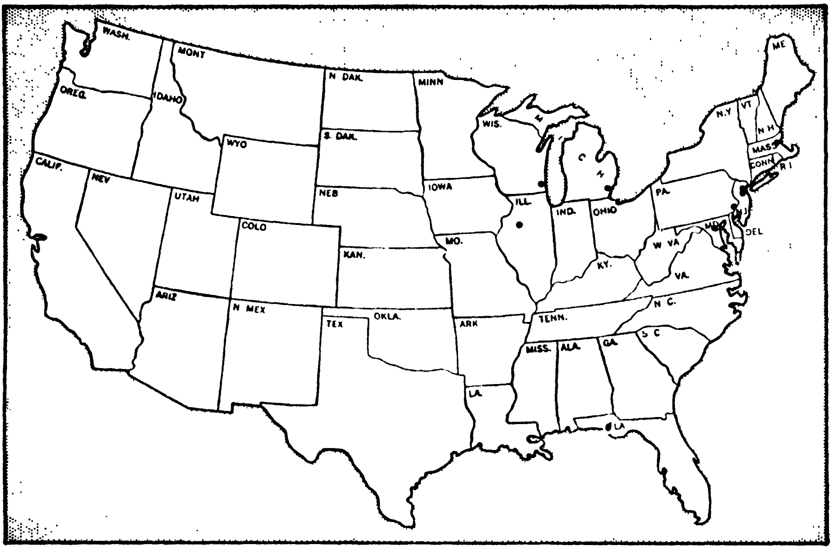
Grades. *n*-, iso-, and *sec*-amyl acetate are commercially important. The last is sold as a technical grade (85 to 88 per cent). Normal and isoamyl acetate and mixtures are generally sold in four grades: Commercial (85 to 88 per cent), flash point 63 to 70°F; high test (85 to 88 per cent), flash point 84°F; technical (90 to 95 per cent), flash point 79°F; and pure (95 to 99 per cent), flash point 77°F.

Containers and Regulations. Tank cars, drum cars, drums, cans, and bottles. Red ICC shipping label required for all grades except high-test *n*-amyl acetate and technical secondary amyl acetate.

Economic Aspects

Amyl acetate, popularly known as banana oil, is largely used as a high-boiling solvent constituent of lacquers and other coating materials. Since the advent of penicillin manufacture, fairly large quantities have been used in the solvent extraction of penicillin from fermentation broth (see *Penicillin*). It is quite possible, however, that other solvents may displace at least a portion of the amyl acetate so used at any time. Necessary equipment for amyl acetate manufacture is quite simple and can be used alternately for the manufacture of other esters, such as butyl acetate. A 2,000-gal kettle equipped with a fractionating column can produce 1,000 lb ester per day (350,000 lb per yr). Very small producers can use the same type of equipment, needing only a small kettle and column.

At least one manufacturer makes amyl acetate by a continuous process which offers obvious economic advantages for large-scale production. In either case, facilities for disposing of dilute waste sulfuric acid must be available.

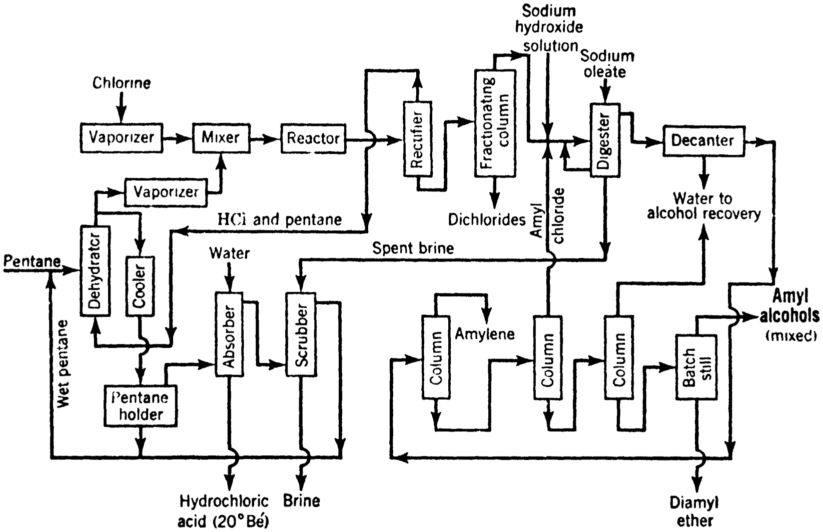


Location of Amyl Acetate Plants

AMYL ALCOHOL

$C_5H_{11}OH$

From Pentane



Reaction

$$C_5H_{12} + Cl_2 \rightarrow C_5H_{11}Cl + HCl$$

$$C_5H_{11}Cl + NaOH \rightarrow C_5H_{11}OH + NaCl$$

60% yield (based on pentane)

Material Requirements

Basis—1 ton amyl alcohols

Pentane	2,700 lb	Sodium hydroxide	1,350 lb
Chlorine	2,500 lb	Sodium oleate	Negligible

Process

The continuous chlorination of pentanes and subsequent alkaline hydrolysis (also continuous) yield amyl alcohols.

Normal and isopentane, obtained from the lower-boiling fractions of natural gasoline, are saturated with hydrogen chloride (from the cycle of operations) and passed at 75 psi through a vaporizer at 85°C. The vapors are introduced into a Venturi mixer where they come into contact with chlorine vapors. Chlorine is supplied at a pressure of 60 psi and a temperature of 50°C. At a volume ratio of 15 parts of pentane to 1 part of chlorine, the gases are mixed at a very high velocity (above 60 mph to minimize the danger of ignition) and are led through a heat exchanger into a reactor maintained at 250 to 300°C.

The reacted gases, which are essentially chlorine-free, are passed through a heat exchanger and a cooler before entering a rectifying tower. Here the gases are refluxed with pentane which serves to condense most of the organic vapors. Hydrogen chloride and some uncondensed pentane pass from the rectifier through a dehydrator where the gases bubble through incoming pentane. The hydrogen chloride combines with the water in the pentane and substantially dehydrates it. The gases are cooled, and part of the pentane runs into a pentane holder for re-use. The hydrogen chloride gas is absorbed with water to give hydrochloric acid. The remaining hydrogen chloride is removed by scrubbing with spent brine from the digesters and the chloride-free pentane is returned to the dehydrator for re-use.

The condensed chlorinated pentanes, from the bottom of the rectifier, are passed to a fractionating column where the monochloropentanes (amyl chlorides) are separated from the dichlorides. About 5 per cent dichloride is formed by the reaction. The isomeric amyl chlorides are then passed to the hydrolyzing units. Chlorination of pentanes yields various monochloride isomers such as the following: from *n*-pentane about 24 per cent primary and 76 per cent secondary amyl chlorides are formed; isopentane yields about 50 per cent primary, 28 per cent secondary, and 22 per cent tertiary amyl chlorides.

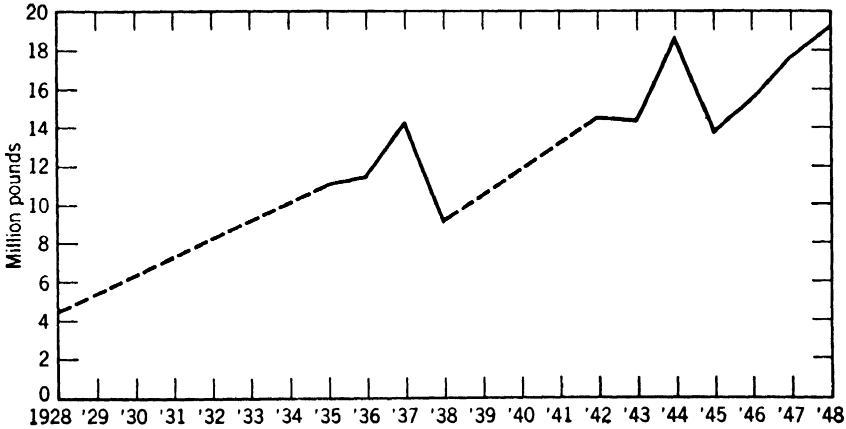
The amyl chlorides are charged into a series of digesters with a solution of sodium hydroxide, sodium oleate, and water. The sodium oleate serves as an emulsifying agent and a catalyst for the topical hydrolysis. The mixture is emulsified and circulated through the digesters at 175°C. About 2 per cent of the chloride is hydrolyzed during each cycle.

The vapors from the hydrolysis are passed into fractionating columns where four or five fractions are separated. The first fraction, amylene, may be hydrated to amyl alcohol. The unchanged amyl chlorides are returned to the hydrolyzer. The alcohol mixture is fed into a third column where most of the water is removed along with some alcohol. The dilute alcohol goes to recovery units.

The bottoms from the third column, crude amyl alcohols, are fed into a batch still where the isomeric mixture is fractionated. Various fractions are taken such as solvent mixtures and special cuts of substantially pure isomer. The residue consists of a high-boiling diamyl ether mixture, a by-product from the hydrolysis reaction, and the mixture of amyl alcohol consists of essentially five isomers of which the three primary alcohols predominate. These are *n*-amyl alcohol (1-pentanol), isoamyl alcohol (3-methyl-1-butanol), and active amyl alcohol (2-methyl-1-butanol). The secondary amyl alcohols which are also present are diethylcarbinol (3-pentanol) and methylpropylcarbinol (2-pentanol). This mixture is marketed as synthetic commercial amyl alcohol under the trade name Pentasol. The isomers may be separated by distillation and chemical processing. Of these isomers, the primary *n*-amyl alcohol is the most important. Varying amounts of tert-amyl alcohol (2-methyl-2-butanol) are obtained in this process, depending primarily on the amount of isopentane in the raw material. It is generally obtained as the overhead in the last column prior to taking the commercial amyl alcohol mixture. The yield of mixed amyl alcohols based on the pentane content of the raw material is about 60 per cent.

From Fusel Oil

Fusel oil is obtained as a by-product in carbohydrate fermentations to produce alcohol (see *Ethyl Alcohol*). The material varies widely in composition, depending on the fermentation raw material, but contains chiefly isoamyl alcohol and active amyl alcohol; isobutyl alcohol (20 per cent), *n*-propyl alcohol (3 to 5 per cent); and small amounts of other alcohols, esters, and aldehydes. The oil is treated chemically and re-

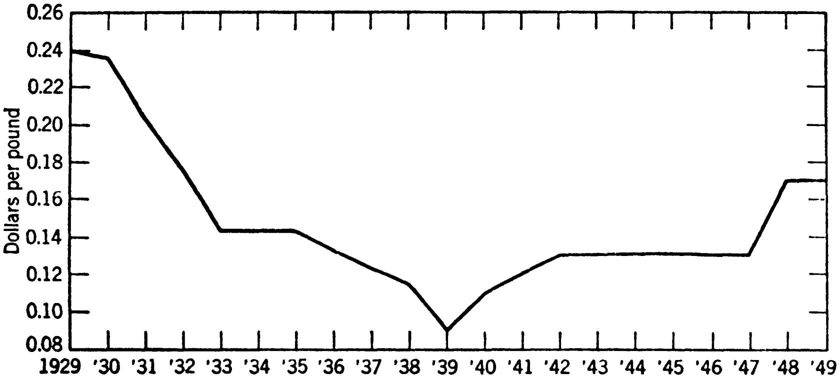


Production—Amyl Alcohols

fined by distillation. All the afore-mentioned alcohols are recovered, with the amyl alcohols, especially isoamyl, predominating. Refined amyl alcohol from fusel oil contains about 85 per cent isoamyl and 15 per cent active amyl alcohol.

Use Pattern

	Per cent
Amyl acetate (all grades)	50
Lacquers and solvents	30
Miscellaneous	20
	100



Price—Amyl Alcohol (From pentane since 1933)

Miscellaneous

Properties. *n-Amyl alcohol* (pentanol-1) (*n*-butylcarbinol) (CH_3-$CH_2CH_2CH_2CH_2OH$). Colorless liquid with a mild characteristic odor.

Mol. wt.	88.15	M.P.	−79°C
Sp. gr.	0.824 20°C/20	B.P.	138.1°C

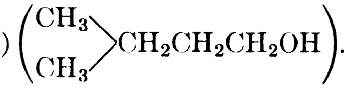
Weight per gallon 6.86 lb

Soluble in alcohol and ether in all proportions at room temperature. Slightly soluble in water (2.7 g per 100 ml at 22°C).

Flash point (closed cup)	100°F
Ignition temperature	700°F
Vapor density (air = 1)	3.04
Explosive limits (% by volume in air)	Lower 1.2

Grades. Technical and C.P.

Containers and Regulations. Tank cars, drums, cans, and bottles. No ICC shipping label required.

Properties. *Primary isoamyl alcohol* (isoamyl alcohol) (3-methyl-1-butanol)  $\left(\begin{matrix}CH_3\\CH_3\end{matrix}>CH_2CH_2CH_2OH\right)$. Colorless liquid with a mild odor.

Mol. wt.	88.15	M.P.	−117.2°C
Sp. gr.	0.813 15°C/4	B.P.	132.0°C

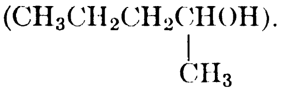
Weight per gallon 6.79 lb

Soluble in alcohol and ether in all proportions at room temperature. Slightly soluble in water (2 g per 100 ml at 14°C).

Flash point (closed cup)	114°F
Ignition temperature	650°F
Vapor density (air = 1)	3.04

Grades. Technical (synthetic), water-white, 4°C distillation range; crude fusel oil (colorless oily liquid with disagreeable odor, chiefly isoamyl alcohol, B.P.—60 per cent between 122 and 138°C, 6.92 lb per gal); refined fusel oil (about 85 per cent isoamyl alcohol and 15 per cent active amyl alcohol, colorless, 6°C boiling range, 6.76 lb per gal at 20°C).

Containers and Regulations. Tank cars, drums, cans, and bottles. No ICC shipping label is required.

Properties. *sec-Amyl alcohol* (methylpropylcarbinol) (pentanol-2)  $(CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HOH)$. Colorless liquid.

Mol. wt.	88.15		
Sp. gr.	0.811 20°C/20	B.P.	119.3°C

Weight per gallon 6.75 lb (20°C)

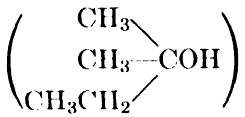
Soluble in alcohol and ether in all proportions at room temperature. Slightly soluble in water (16.6 g per 100 ml at 20°C).

Flash point (open cup)	105°F
Ignition temperature	650°F
Vapor density (air = 1)	3.04

Grades. Technical.

Containers and Regulations. Tank cars, drums, cans, and bottles. No ICC shipping label required.

Properties. *tert-Amyl alcohol* (dimethylethylcarbinol)



$$\left(\begin{matrix}CH_3\diagdown\\CH_3—COH\\CH_3CH_2\diagup\end{matrix}\right)$$

Colorless liquid with a camphor-like odor.

Mol. wt.	88.15	M.P.	−11.9°C
Sp. gr.	0.809 20°C/4	B.P.	102°C

Weight per gallon 6.75 lb

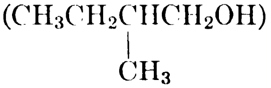
Soluble in alcohol and ether at room temperature. Slightly soluble in water.

Flash point (closed cup)	67°F
Vapor density (air = 1)	3.03

Grades. Technical and C.P.

Containers and Regulations. Drums, cans, and bottles. Red ICC shipping label is required.

Properties. *Active amyl alcohol* (*sec*-butylcarbinol)



$$(CH_3CH_2\underset{\substack{|\\CH_3}}{C}HCH_2OH)$$

Colorless liquid.

Mol. wt.	88.15		
Sp. gr.	0.816 20°C/4	B.P.	128°C

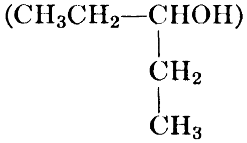
Weight per gallon 6.8 lb

Soluble in alcohol and ether in all proportions at room temperature. Slightly soluble in water (3.6 g per 100 g at 30°C).

Grades. Technical.

Containers and Regulations. Drums, cans, and bottles. No ICC shipping label required.

Properties. *sec-Amyl alcohol* (diethylcarbinol) (pentanol-3)



$$(CH_3CH_2\text{—}\underset{\substack{|\\CH_2\\|\\CH_3}}{C}HOH)$$

Colorless liquid.

Mol. wt.	88.15		
Sp. gr.	0.815 25°C/4	B.P.	115.6°C

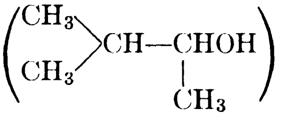
Weight per gallon 6.83 lb

Soluble in alcohol and ether at room temperature. Slightly soluble in water (5.5 g per 100 g at 30°C).

Grades. Technical.

Containers and Regulations. Tank cars, drums, cans, and bottles. No ICC shipping label is required.

Properties. *sec-Isoamyl alcohol*



$$\left(\begin{array}{l} CH_3 \\ CH_3 \end{array}\!\!> CH-\underset{\underset{\displaystyle CH_3}{|}}{CHOH}\right)$$

Mol. wt.	88.15		
Sp. gr.	0.819 (19°C)	B.P.	113 to 114°C

Soluble in alcohol and ether in all proportions at room temperature. Slightly soluble in water (2.8 g per 100 g at 30°C).

Flash point (closed cup)	103°F
Vapor density (air = 1)	3.04

Properties. *Amyl alcohol* (2,2-dimethylpropanol-1) [$(CH_3)_3CCH_2$-OH]. Colorless crystals.

Mol. wt.	88.15	M P.	53°C
Sp. gr.	0.812 20°C/4	B.P.	114°C

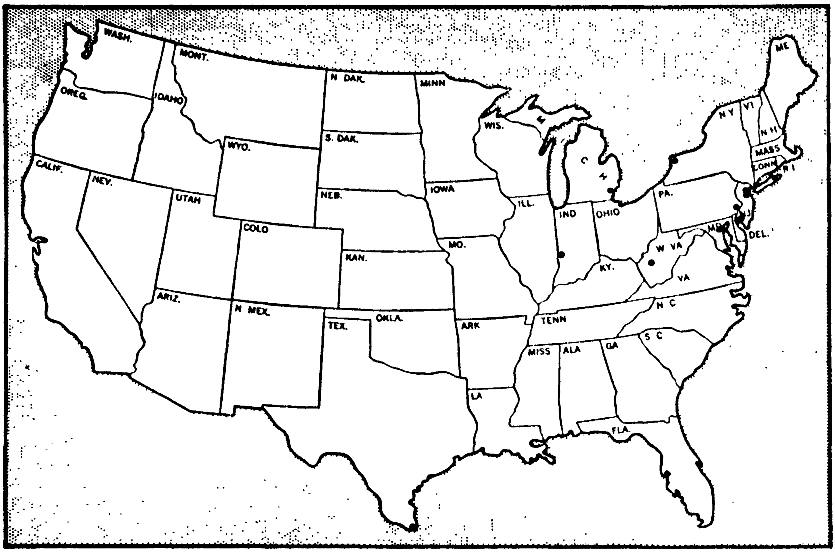
Soluble in alcohol and ether in all proportions at room temperature. Slightly soluble in water.

Economic Aspects

Until the late 1920's, all five-carbon alcohols were produced in comparatively small quantities by the fractionation of fusel oil recovered from alcoholic-fermentation liquors. In this case, the alcohols were principally isoamyl and "active" amyl alcohols. Normal amyl alcohol was practically a laboratory curiosity. The development of a commercial process for the controlled chlorination of pentanes from natural gasoline and subsequent hydrolysis of the chlorinated hydrocarbon soon made *n*-amyl alcohol an important industrial solvent. The process is comparatively simple chemically, but great care must be taken to control the chlorination step to avoid explosion. The chlorination step produces various polychlorinated hydrocarbons as by-products, and the hydrolysis step yields some diamyl ether and amylenes. The sole large-scale manufacturer has built an entire industry around pentane chlorination to yield a wide variety of amyl compounds. This plant is said to have a capacity of more than 10,000,000 lb of amyl alcohols per yr.

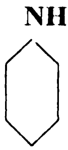
Secondary amyl alcohol is now manufactured by the hydration of amylene in a manner similar to the manufacture of other secondary alcohols (see *Isopropyl Alcohol*).

Larger supplies of both *n*-amyl alcohol and isoamyl alcohol are expected to be available in the near future when recovery of various by-product alcohols from the Fischer–Tropsch synthetic-fuel plants is initiated.

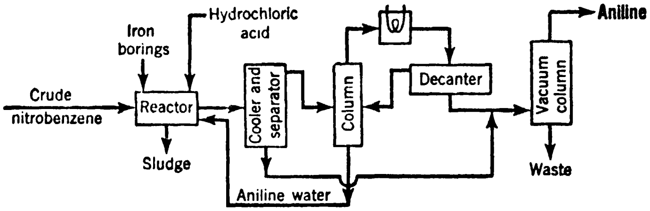


Location of Amyl Alcohol Plants

ANILINE



From Nitrobenzene by Reduction



Reaction

$$4C_6H_5NO_2 + 9Fe + 4H_2O \xrightarrow{HCl} 4C_6H_5NH_2 + 3Fe_3O_4$$

90–95% yield

Material Requirements

Basis—1 ton aniline

Nitrobenzene	2,780 lb
Iron borings	3,200 lb
Hydrochloric acid (30%) *	250 lb

Process

Crude nitrobenzene is charged into a reducer (reactor) fitted with an efficient reflux condenser. The reducer is a steam-jacketed cast-iron enclosed cylindrical vessel containing an agitator. Cast-iron borings (turnings) or powder (free from oil and nonferrous metals), water, and catalyst are added gradually, in small quantities, to the nitrobenzene. Generally, 10 to 20 per cent of the total iron is added at the beginning, and the mixture is heated by steam to reflux temperature (*ca.* 200°C). The remaining iron is added over a period of time at a rate determined by the proper temperature–pressure balance. The addition rate is fast enough to maintain lively reflux by the heat generated from the exothermic reaction, yet slow enough to prevent excessive hydrogen pressure buildup.

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* Or equivalent aniline salt mother liquor.

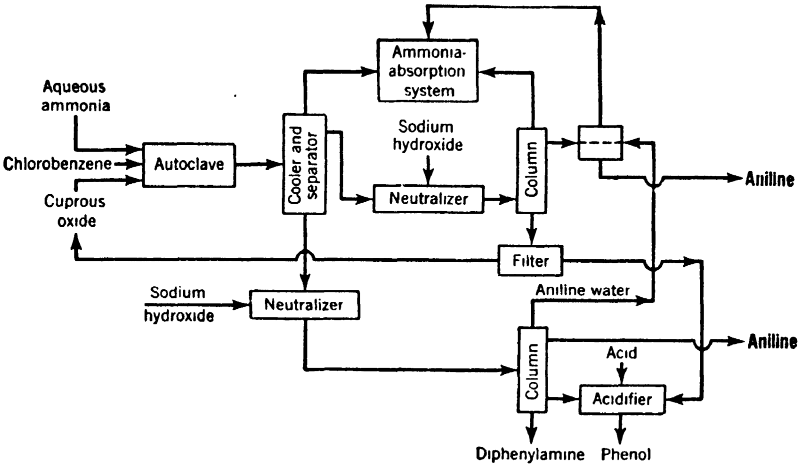
The water required for the reaction is generally in the form of aniline water recovered from the separator or column and is added to the reducer either in bulk at the start or in small quantities along with the iron additions. Dilute (30 per cent) hydrochloric acid is added along with the water as catalyst. The acid reacts with the iron borings, forming catalytically active iron salts. Subsequent runs may utilize the aniline–hydrochloric acid mother liquor as the source of the catalyst and some of the reaction water. The weight ratio of reactants is approximately 115 parts of iron borings, 0.27 part of 100 per cent hydrochloric acid, and 60 parts of water per 100 parts of nitrobenzene. After the last iron addition, the reaction is heated with steam to maintain lively reflux.

At the end of the reduction (about 10 hr for a 5,000-lb charge), the aniline is separated from the reducer charge by one or more of several methods. The liquid water–aniline mixture may be separated from the solid iron oxide–iron hydroxide sludge by steam distillation, vacuum distillation, filtration, centrifugation, or syphoning. For example, the finished reduction product may be neutralized with a small amount of sodium carbonate (about equal to the amount of hydrochloric acid in the charge) and allowed to settle. Most of the aniline and some water are syphoned off, and the residual aniline is separated from the sludge by steam distillation. The sludge consisting of ferric oxide, water, and small amounts of ferric hydroxide is dumped and may be marketed after drying.

The water–aniline mixture from the reducer is run to a separator, where the heavier aniline separates and is withdrawn from the bottom. The top layer, which contains 3 to 5 per cent aniline, is partially distilled until the aniline content in the water is low. The residual aniline water is returned to the reducer for subsequent runs. The aniline in the distillate is separated by decantation, and the water layer is redistilled to obtain the remaining aniline. An alternate procedure is to extract the aniline from the aniline water with nitrobenzene.

The aniline streams from the separator and decanter are united and vacuum-distilled to yield purified aniline. The yield based on nitrobenzene is approximately 95 per cent by weight.

From Chlorobenzene by Ammonolysis



Reaction

$$C_6H_5Cl + 2NH_3 \text{ (aqua)} \rightarrow C_6H_5NH_2 + NH_4Cl \text{ (sol'n)}$$

85–90% yield

Material Requirements (Major)

Basis—1 ton aniline

Chlorobenzene	2,750 lb
Ammonia solution (28%)	7,450 lb
Cuprous oxide	350 lb

Process

Chlorobenzene is charged into a series of horizontal, rotating, high-pressure rolled steel autoclaves. Approximately 0.1 mole of cuprous oxide and 4 to 5 moles of 28 to 30 per cent aqueous ammonia per mole of chlorobenzene are added. The reaction is initiated at a temperature of 180°C and is later maintained at 210 to 220°C under constant agitation. The pressure rises to 750 to 850 psi. The active catalyst is cuprous chloride produced from cuprous oxide by the by-product ammonium chloride as follows:

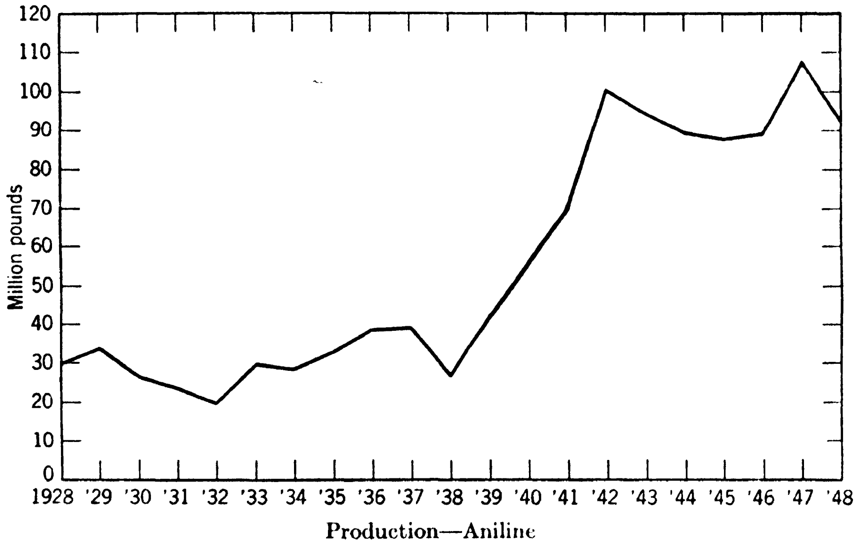
$$Cu_2O + 2NH_4Cl \rightarrow Cu_2Cl_2 + 2NH_3 + H_2O$$

A large excess of ammonia solution is used to suppress the phenol-producing side reaction ($C_6H_5Cl + NH_3 + H_2O \rightarrow C_6H_5OH + NH_4Cl$). If the indicated ratio of reactants is used, the rate of aniline formation is about 20 times greater than the rate of phenol formation.

The reaction products are cooled below 100°C and run to a separator. The free ammonia continues to an absorption and condensing system for recovery. The settled reaction mass separates into two layers, an aniline-rich lower layer and an aqueous upper layer. The approximate distribution of reaction products (not including unreacted chlorobenzene) in the two layers is: aniline layer—82 per cent aniline, 5 per cent phenol, and 1 per cent diphenylamine; water layer—5 per cent aniline, 0.5 per cent phenol, 9 per cent chloride ion (NH_4Cl), 3 per cent cuprous oxide, and 14 per cent ammonia.

The aqueous layer is drawn from the top of the separator and is run to a neutralizer, where it is treated with sodium hydroxide or lime. A sufficient amount of alkali is used to react with the ammonium chloride and phenol. The solution is fractionally distilled, and the liberated ammonia expelled first is recovered in an absorption system. The second fraction consists of aniline and water which are separated by decantation. The residual solution of sodium phenate and sodium chloride is filtered to remove the precipitated copper oxides, which are re-used in subsequent runs.

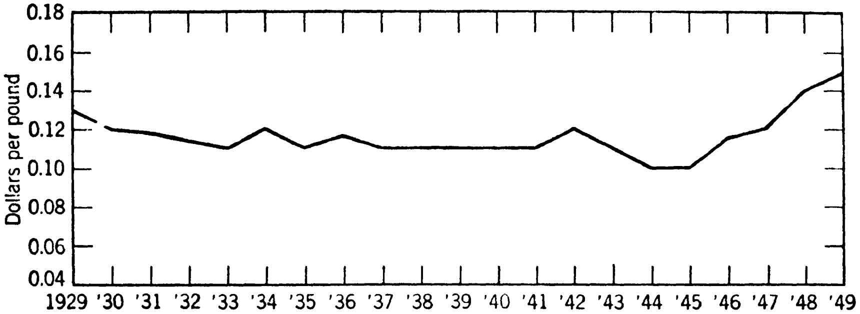
The aniline layer is withdrawn from the bottom of the separator and treated with 50 per cent sodium hydroxide solution. Approximately 0.2 per cent of the volume of the aniline layer is used. The solution is fractionally distilled, yielding first an aniline–water mixture, which is further treated as described previously. The second fraction is technically pure (97 to 99 per cent) aniline. The residue is steam-distilled, yielding diphenylamine. The phenol is recovered by acidifying the residue (mostly sodium phenate) and distilling. The yield of aniline is 85 to 90 per cent based on chlorobenzene.



Production—Aniline

Use Pattern

	Per cent
Rubber chemicals	50
Dyes and intermediates	30
Miscellaneous	20
	100



Price—Aniline

Miscellaneous

Properties. Colorless, oily liquid, which rapidly turns brown on exposure to air and light.

Mol. wt.	93.12	M.P.	−6.2°C
Sp. gr.	1.0236 20°C/20	B.P.	184.4°C

Weight per gallon 8.52 lb (20°C)

Soluble in alcohol and ether. Slightly soluble in water (3.6 g per 100 ml at 18°C).

Flash point (open cup)	195°F
Ignition temperature	1,000°F
Vapor density (air = 1)	3.22

Grades. Commercial and C.P.

Containers and Regulations. Tank cars, drums, and bottles. Considered a class B poison and requires a "Poison" ICC shipping label.

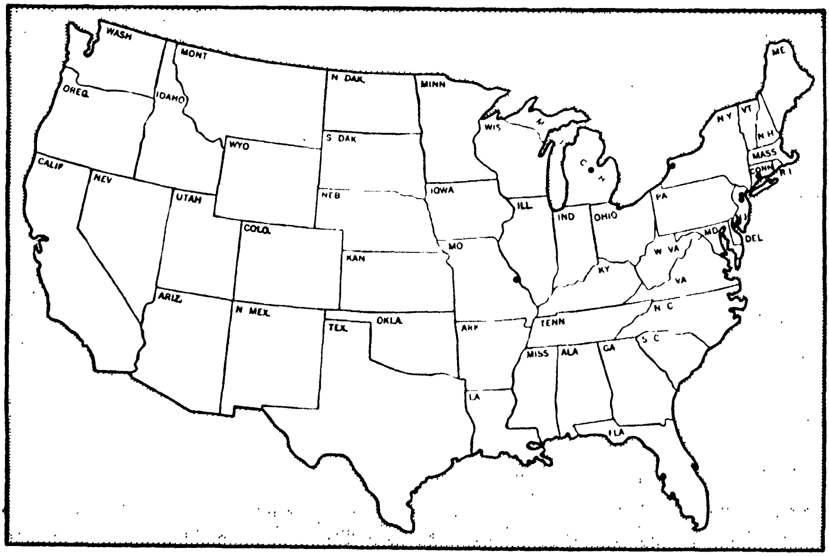
Economic Aspects

The manufacture of aniline is an old art tied in closely with dye manufacture, which industry used the major production of aniline for many years. In wartime, demand for aniline rises as an intermediate in the manufacture of diphenylamine for smokeless powder and in the manufacture of tetryl. In World War II the manufacture of synthetic-rubber additives such as diphenylamine, hydroquinone, and cyclohexylamine required large quantities. This latter market will doubtless remain, but it must compete with amines made from other raw materials.

The old batch method of manufacturing aniline from nitrobenzene is still used to a great extent (75 per cent of production), with numerous variations in aniline recovery from the reacted charge. Steam distillation of the entire charge is costly and has been largely superseded by mechanical separation of the aniline layer and steam sparging of the remaining slurry. Yield is important, however, since raw materials represent about 75 per cent of the total product cost. Accordingly, an economic balance must be made between aniline recovery and steam costs.

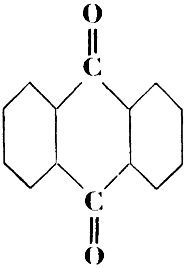
In the batch process, reducers of at least 1,500 gal capacity are preferred for economic operation. Normal plant sizes vary from 4,000,000 to 20,000,000 lb annual capacity, but plants of 50,000,000 lb yearly production are known. A 10,000,000-lb plant costs about $100 per 1,000 lb annual capacity.

The continuous process of ammonolysis of chlorobenzene is competitive with the older batch process and offers natural operating economies which are minimized by the importance of raw-material costs. A number of patents have been granted on the vapor-phase hydrogenation of nitrobenzene, but the process is not widely used.

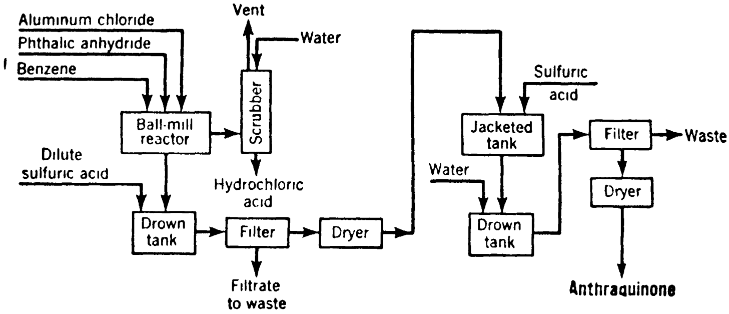


Location of Aniline Plants

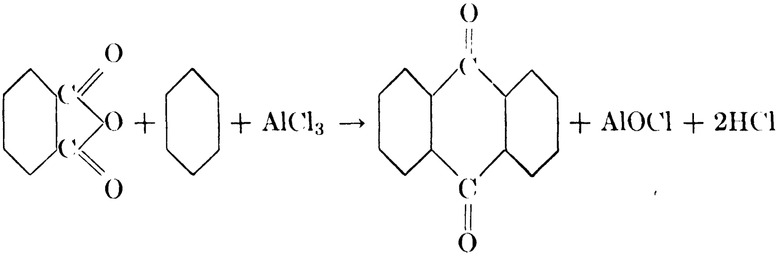
ANTHRAQUINONE



From Phthalic Anhydride and Benzene



Reaction



Phthalic anhydride Benzene Anthraquinone

95% yield

Material Requirements

Basis—1 ton anthraquinone

Phthalic anhydride	1,500 lb	Sulfuric acid (98%)	10,000 lb
Benzene	790 lb	Aluminum chloride	2,800 lb

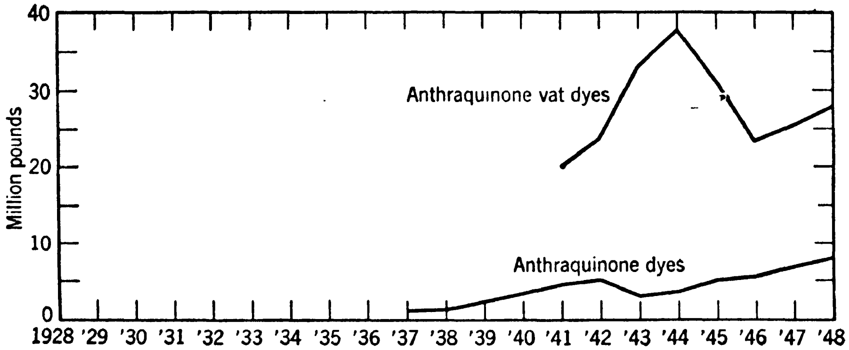
Process

Phthalic anhydride, benzene, and aluminum chloride in molar proportions 1:1:2 are charged into a reactor, which is essentially a horizontal ball mill containing iron balls or rods and is equipped with a tail pipe for removing hydrogen chloride formed during the reaction. The reaction is carried out at 40 to 50°C, during which time the charge swells, forming an aluminum chloride complex of benzoyl–benzoic acid. Liberated hydrogen chloride is absorbed in a scrubbing system. At the end of the reaction the dry powder remaining in the reactor is dropped into a tank containing chilled dilute sulfuric acid. The aluminum chloride complex decomposes, and *o*-benzoyl–benzoic acid precipitates. The precipitated acid is filtered, washed, and dried. The yield based on phthalic anhydride approximates 96 per cent.

The dried *o*-benzoyl–benzoic acid (1 part) is dissolved in 98 per cent sulfuric acid (4 parts) in a jacketed vessel in which the charge is heated for 1 to 3 hr at 115 to 150°C. At the end of the reaction period the charge is dropped into a tank of boiling water. The resulting slurry is allowed to cool and is then filtered, washed, and dried. The yield of anthraquinone from the *o*-benzoyl–benzoic acid is better than 99 per cent. For further purification the product may be sublimed.

Other Processes

Anthraquinone has been made in the past by oxidizing a suspension of purified anthracene in boiling water with sodium dichromate and sulfuric acid. The resulting anthraquinone is contaminated with anthracene and requires extensive purification.



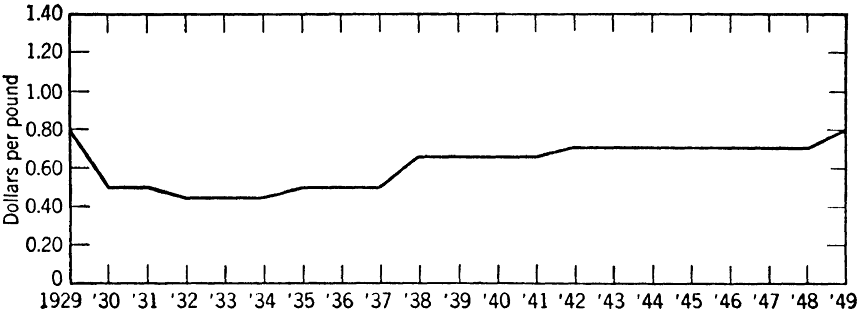
Production—Anthraquinone Dyes

An electrolytic method has also been used for the oxidation of anthracene. In this process a suspension of anthracene in 20 per cent sulfuric acid is electrolytically oxidized in the presence of 2 per cent ceric sulfate at 70 to 100°C. A platinum anode is used with a current density of 46 to 47 amperes per square foot and a voltage drop across the cell of 2.8 to 3.5 volts.

A catalytic vapor-phase oxidation process similar to that used for phthalic anhydride manufacture (*q.v.*) has been proposed. In this process vaporized anthracene reacts with air in the presence of a supported vanadium pentoxide catalyst at 400°C. The process is apparently not used industrially.

Use Pattern

Dye manufacture	100 per cent



Price—Anthraquinone

Miscellaneous

Properties. Yellow needles.

Mol. wt.	208.20	M.P.	Sublimes at 286°C
Sp. gr.	1.438 20°C/4	B.P.	379 to 381°C

Soluble in alcohol (0.05 per cent at 18°C, 2.25 per cent hot), acetone, and hot benzene. Very slightly soluble in ether. Insoluble in water.

Flash point (closed cup)	365°F
Vapor density (air = 1)	7.16

Grades. Technical, sublimed, and 30 per cent paste (sold on 100 per cent basis).

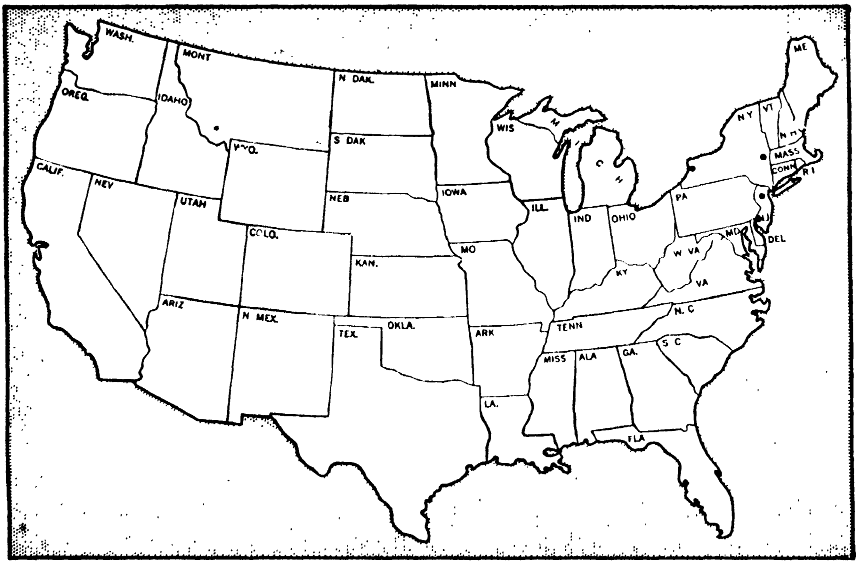
Containers and Regulations. Barrels and bottles. No ICC shipping label required.

Economic Aspects

Anthraquinone is produced almost entirely by manufacturers of dyes and other dye intermediates. Before World War I, little was made in the United States. The only process used was sodium dichromate oxidation of anthracene, which involved careful and expensive purification of the reacted mass. An electrochemical method in which anthracene is anodically oxidized has also been used but is apparently uneconomic. Some anthraquinone has been made on a small scale by the catalytic vapor-phase oxidation of anthracene. This was also costly because anthracene is always contaminated with carbazole, which must be completely burned to carbon dioxide and water. The resulting anthraquinone must still be refined by sulfuric-acid treatment. The most widely used process, in which benzene and phthalic anhydride are condensed, produces a pure product apparently much more economically than the other processes.

Production figures for anthraquinone are not available, and so the production of anthraquinone dyes and anthraquinone vat dyes is shown on the production chart. All such dyes do not use anthraquinone as a raw material, but their production trend probably parallels that of anthraquinone. In some important cases chloroanthraquinone is used as the intermediate for dye manufacture. This intermediate is manufactured from phthalic anhydride and chlorobenzene in the same type of equipment that is used for anthraquinone manufacture.

The peak production of anthraquinone vat dyes during the war years was occasioned by demand for dyes for military uniforms, canvas, and similar textiles.

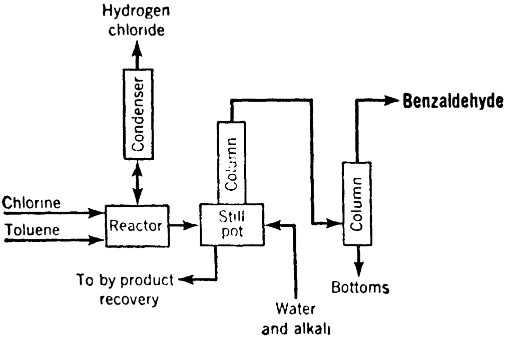


Location of Anthraquinone Plants

BENZALDEHYDE

C_6H_5CHO

Chlorination of Toluene



Reaction

$$C_6H_5CH_3 + 2Cl_2 \longrightarrow C_6H_5CHCl_2 + 2HCl$$

$$C_6H_5CHCl_2 + H_2O \xrightarrow[\text{alkali}]{\text{Acid or}} C_6H_5CHO + 2HCl$$

75–85% yield

Material Requirements

Basis—1 ton benzaldehyde

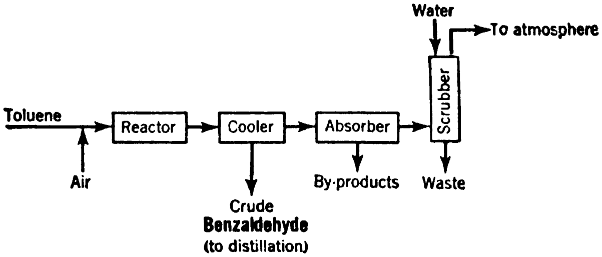
Toluene	2,180 lb
Chlorine	3,580 lb

Process

Dry chlorine is passed into boiling toluene (110°C) until the reaction mass reaches a specific gravity of 1.283 under which conditions the greatest percentage of benzal chloride is formed. Because of nonuniform chlorination, small percentages of benzyl chloride and benzotrichloride and much smaller amounts of ring-chlorinated products are also formed. The presence of iron and other impurities such as factory dust tends to catalyze nuclear substitution. It is, therefore, important to eliminate these impurities as well as to utilize glass- or lead-lined reaction vessels. Catalytic agents (for side-chain chlorination) such as phosphorus tri- or pentachloride (about 2 per cent based on the weight of toluene) or sunlight may be used, but generally the reaction proceeds rapidly enough in the absence of such agents. A reflux condenser is used on the reaction kettle to keep the boiling toluene from escaping. Because the reaction is exothermic, no outside heating is necessary after initiation. Hydrogen chloride, evolved during the chlorination, is led through the condenser and recovered by absorption in water.

The reaction mass (crude benzal chloride) is introduced into a still pot where it is treated with boiling water (plus a small percentage of either acid or alkali such as calcium hydroxide or carbonate) to yield crude benzaldehyde. Benzoic acid and chlorobenzaldehyde are also obtained as the accompanying by-products are hydrolyzed. The benzaldehyde is separated by steam distillation and is then further purified by distillation through a fractionating column. The product obtained is better than 98 per cent pure.

Oxidation of Toluene



Reaction

$$C_6H_5CH_3 + O_2 \text{ (air)} \xrightarrow{\text{Catalyst}} C_6H_5CHO + H_2O$$

30–50% yield

Material Requirements

Basis—1 ton benzaldehyde

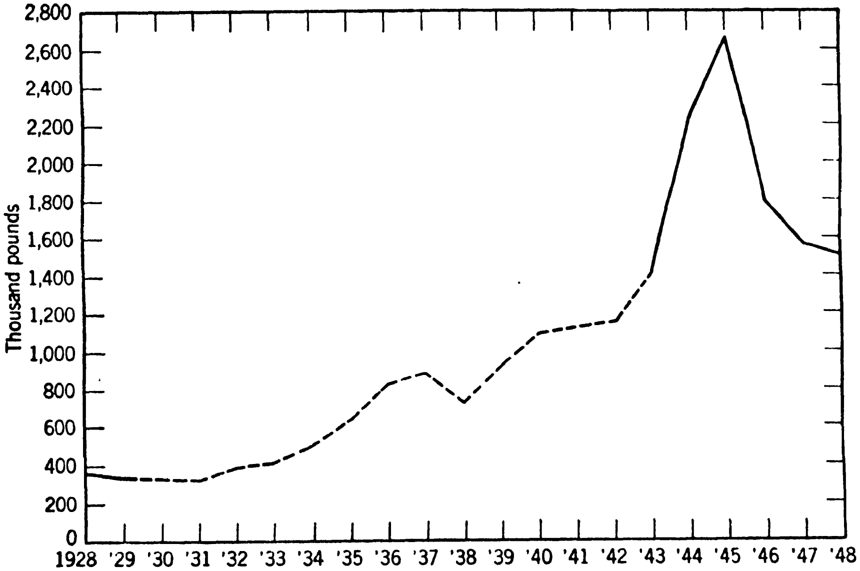
Toluene	4,350 lb
Air	60,400 lb
Catalyst	Small

Process

Toluene is directly oxidized in the vapor phase at atmospheric pressure by a mixture of air and toluene vapor (14-to-1 weight ratio) being blown through a catalyst maintained at approximately 500°C. The reaction is exothermic, and so efficient heat transfer must be provided.

The catalysts generally used consist of oxides of metals belonging to the fifth or sixth groups of the periodic system. A mixture of uranium oxide (93 per cent) and molybdenum oxide (7 per cent) impregnated on a pumice or asbestos carrier is claimed to give relatively high yields of benzaldehyde with low percentages of toluene going to complete combustion. The addition of small amounts of copper oxide to the catalyst mixture reduces by-product maleic anhydride formation.

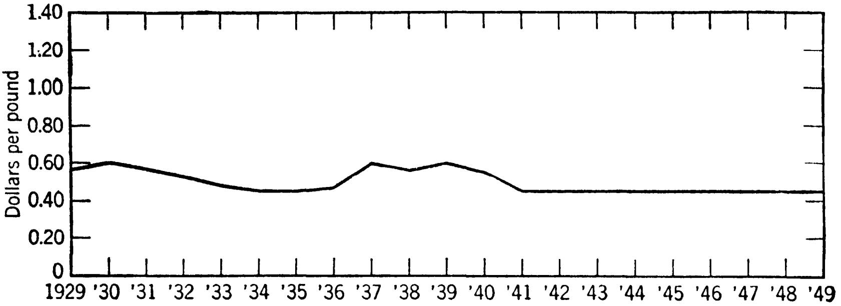
The hot reaction gases are cooled to remove the condensable products; the noncondensed gases are recirculated after further addition of toluene and air to maintain the proper mixture ratio. There is a varying amount of by-product formation during the oxidation. The principal by-products are maleic anhydride, benzoic acid, anthraquinone, complex high-boiling oils of unknown composition, carbon monoxide, carbon dioxide, and water. The separation and isolation of these various constituents from benzaldehyde in the reaction gases may be accomplished by passing the gases through a series of condensers maintained at different temperatures. The gases are then passed through activated carbon adsorbers and are scrubbed with water before release to the atmosphere. The crude benzaldehyde is distilled to yield a product of greater than 98 per cent purity. Conversion per pass approximates 10 to 20 per cent benzaldehyde; the over-all yield is about 30 to 50 per cent by weight based on the toluene used.



Production—Benzaldehyde (Technical)

Use Pattern

Dyes and dye intermediates	No breakdown available
Flavors, foods, and cosmetics	
Drugs and pharmaceuticals	
Miticide	
Miscellaneous	



Price—Benzaldehyde (Technical)

Miscellaneous

Properties. Colorless, strongly refractive liquid with a characteristic aromatic odor resembling bitter almonds.

Mol. wt.	106.12	M.P.	−26°C, solidifies at −56°C
Sp. gr.	1.046 20°/4°C	B.P.	179.5°C

Weight per gallon 8.72 lb (20°C)

Volatilizes with steam; 0.3 per cent soluble in water at room temperature. Miscible in all proportions with alcohol and ether at 25°C.

Flash point (closed cup)	148°F
Ignition temperature	377°F
Vapor density (air = 1)	3.66

Grades. Technical and N.F. (98 per cent minimum benzaldehyde).

Containers and Regulations. Stainless-steel drums, glass carboys, and bottles. Containers must be well filled and tightly covered since benzaldehyde easily undergoes oxidation in the presence of air to yield benzoic acid. Industrially, benzaldehyde may be considered nonpoisonous and requires no special ICC shipping label.

Economic Aspects

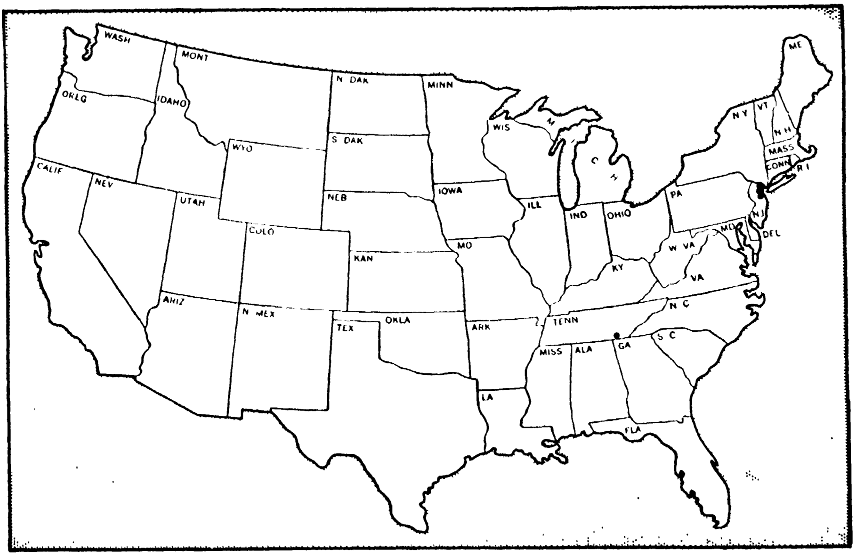
Numerous processes are available for the manufacture of benzaldehyde, and many of these have been used on either a large or a small scale from time to time. For many years, the chief method of benzaldehyde manufacture has been by alkaline hydrolysis of benzal chloride, obtained in turn by the chlorination of toluene. Such a plant is quite flexible in that toluene may be chlorinated to benzyl, benzal and benzochlorides, which in turn may be hydrolyzed to benzyl alcohol, benzaldehyde, and benzoic acid, respectively. Practically all benzoic acid is made today, however, by the decarboxylation of phthalic acid (see *Benzoic Acid*).

Although the hydrolysis process yields as cheap a product as other processes if not a cheaper one, the presence of chlorine in the product makes it unsuitable for use in perfumery. Chlorine-free benzaldehyde may be made by either liquid-phase (with manganese dioxide and sulfuric acid) oxidation or catalytic vapor-phase oxidation of toluene. Both processes yield some benzoic acid as a by-product. Liquid-phase oxidation is the most costly process but can be readily adapted to small-scale manufacture. The most recent process is the condensation of carbon monoxide and benzene under pressure.

Existing plants vary in size from 100,000 lb to 2,000,000 lb per yr. A plant making 150,000 lb annually by the benzal chloride hydrolysis process will cost about $50,000. Larger plants require a smaller investment per annual pound of product.

Like benzoic acid, benzaldehyde uses did not vary greatly before World War II, but the tremendous demand for benzyl benzoate (over 2,000,000 lb in 1945 versus 78,000 lb in 1940) for military ointments and delousing sprays led to greatly increased production during the war.

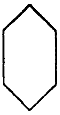
Oil of bitter almonds, containing 96 to 98 per cent benzaldehyde, competes with synthetic benzaldehyde in perfumery but is rapidly being displaced by the synthetic material.



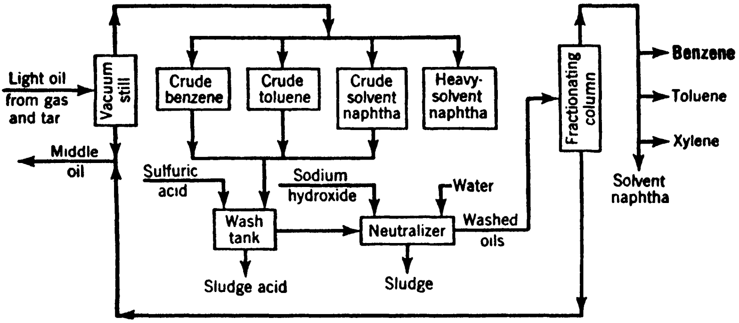
Location of Benzaldehyde Plants

BENZENE

(BENZOL)



From Coal Gas and Tar Light Oil



Yield

One ton of coal yields 1.85 gal benzene (from gas light oil) and 0.1 gal benzene (from tar light oil)

Material Requirements

Basis—1 ton benzene (275 gal)

Light oil	475 gal
Sulfuric acid (66°Bé)	19 lb
Sodium hydroxide (100%)	29–57 lb

Process

Benzene or benzol (the crude product) is obtained by the fractional distillation of light oil, which in turn is formed as a by-product in the high-temperature destructive distillation of coal. The by-product coking of one ton of coal produces approximately 10 gal of tar and 2 to 4 gal of light oil (see *Coke* for details).

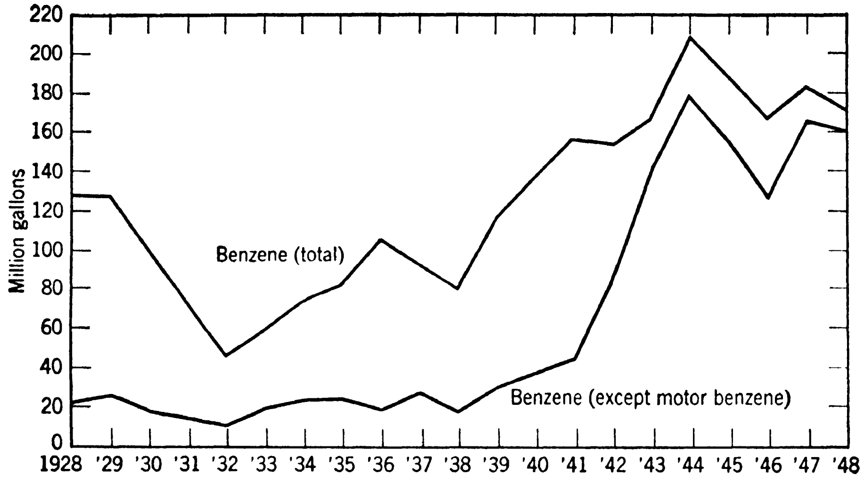
The composition of the coal tar is governed chiefly by the coking and recovery procedures used, but it also varies according to the type of raw coal used. Generally, 8 to 12 gal of tar is obtained per ton of coal pyrolzyed. The tar is fractionally distilled to yield light oils, middle oils, heavy oils, and anthracene oils. See *Naphthalene* for details on coal-tar distillation. The light-oil fraction (distilling up to about 200°C) constitutes approximately 5 per cent of the tar. In other words, a small amount of light oil condenses with the tar, and about 0.5 gal of light oil per ton of coal is realized by tar distillation.

This relatively small amount of light oil is generally added to the major portion (2 to 4 gal) of light oil obtained by scrubbing the coal gas. The coal gas, before scrubbing, contains about 1 per cent by volume of light oil. Broken up into its major constituents, the gas contains about 0.66 per cent by volume benzene, 0.13 per cent toluene, 0.05 per cent xylene, and less than 0.10 per cent of other aromatic hydrocarbons. The recovery of light oil from the coke-oven gas averages 95 per cent.

The combined light oils are usually sent to refiners for further processing. A typical composition of 3.2 gal of light oil (obtained per ton of coal) follows:

	Gal
Benzene	1.85
Toluene	0.45
Xylenes and light-solvent naphthas	0.30
Unsaturated hydrocarbons (acid wash)	0.16
Heavy hydrocarbons and naphthalene	0.24
Wash oil	0.20
	3.20

The crude light oils are charged into continuous, semicontinuous, or batch-fractionating columns ranging from 6,000 to 15,000 gal capacity. For batch operation, the stills are heated with indirect-steam coils at the beginning and later with direct steam to drive over the heavier fractions. If motor benzol is the desired product, only one fraction is taken. This fraction may be washed to remove unsaturates, but generally inhibitors are added to the unwashed distillate to produce specification motor fuel. This consists merely in the addition of small amounts, 0.002 to 0.006 per cent, of an organic antioxidant such as monobenzyl-*p*-aminophenol or butyl-*p*-aminophenol. For separation of light oil into benzene, toluene, xylene, and solvent naphtha, the columns are operated so as to obtain several fractions. The crude cuts are collected and charged individually (except the heavy-solvent naphtha fraction) into a cylindrical, agitated steel wash tank (5,000 to 13,000 gal capacity). Here the fractions are washed with several portions of concentrated sulfuric acid (66°Bé) to remove most of the unsaturated compounds (chiefly mono-olefins), which are discharged from the bottom of the wash tank as sludge acid. This sludge is an intimate mixture of unused acid, entrained light oil, and resins (reaction products), and in modern plants it is the practice to destroy the material by burning. The hydrocarbons (containing entrained acid) are removed from the top of the wash tank and passed to a neutralizer where they are washed first with a dilute solution of sodium hydroxide and then with water. The neutralization may be carried out in the acid wash tank, thereby eliminating additional equipment. Generally, 5 to 8 hr is required to treat a batch of oil, but again this varies widely according to plant procedure. The shrinkage loss, during a typical washing of the light oil, approximates 4 to 6 per cent by volume.



Production—Benzene

The washed products are run to fractionating columns, where they are distilled to yield the various individual components. Generally, indirect-steam-heated batch stills are used; vacuum may be applied to distil the higher-boiling constituents. Benzene, toluene, xylene, and solvent naphtha are obtained in the various standard grades. The pure products are usually dehydrated by passage through beds of activated alumina, calcium chloride, or caustic soda before shipment. See *Toluene* and *Xylene* for further details on these products.

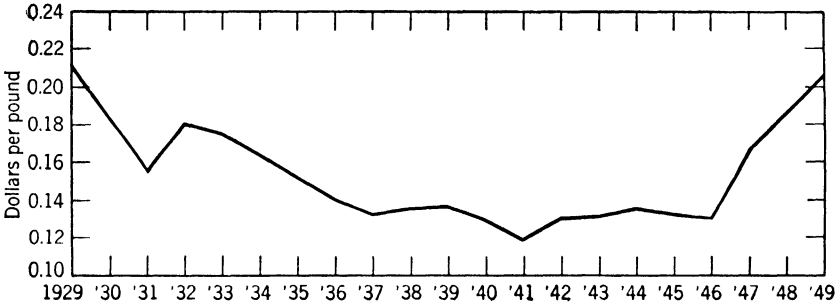
The residues from the pure hydrocarbon stills are usually burned as fuel. Volatile resin oils may be recovered from the residues by steam distillation if economically warranted.

Benzene, constituting 55 to 70 per cent (by volume) of the crude light oil, is obtained in essentially pure form from the fractionating stills. Pure reagent benzene may be obtained by crystallization in batch units designed like standard ice-making machinery. The impurities remain in the mother liquor; the pure benzene freezes (5.5°C). On melting, the reagent grade is obtained.

Benzene may also be produced from petroleum by hydroforming. See *Toluene* for details. Most benzene produced from petroleum, however, is utilized by blending with gasoline to increase its octane rating.

Use Pattern

	1948 (est.), per cent
Phenol	20
Styrene	25
Nylon	10
Detergents	5
Miscellaneous chemicals and solvents (aniline, maleic anhydride, diphenyl, nitrobenzene, chlorobenzenes, etc.)	30
Motor benzol	10
	100



Price—Benzene (Except motor benzol)

Miscellaneous

Properties. Clear, colorless, flammable liquid with a pleasant characteristic odor. Liquid is highly refractive, and the vapors burn with a smoky flame.

Mol. wt.	78.11	M.P.	5.56°C
Sp. gr.	0.879 20°C/4	B.P.	80.1°C

Weight per gallon 7.32 lb

Soluble in alcohol and ether. Slightly soluble in water (0.07 per cent at 22°C).

Flash point (closed cup)	12°F
Ignition temperature	1,076°F
Vapor density (air = 1)	2.77
Explosive limits (% by volume in air)	Lower 1.5 Upper 8.0

Grades. Crude; straw color; inhibited motor benzol, motor benzol; industrial (90 per cent distils below 100°C), industrial pure (2°C); nitration (1°C), USP, and thiophene-free.

Containers and Regulations. Tank cars, drums, pails, cans, and bottles. Red ICC shipping label required.

Economic Aspects

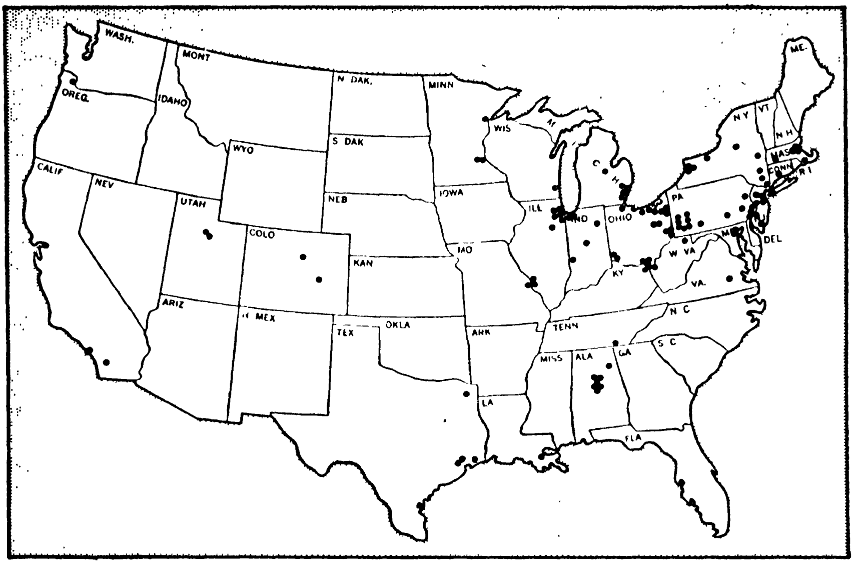
For many years the chief producers of benzol have been the by-product coke and manufactured-gas industries. The coking of coal yields 1.5 to 2.5 gal benzol per ton of coal coked, depending on the grade of coal and the efficiency of light-oil recovery. Chief plant variations are in absorber operation and types of stills used. Naturally the more efficient plants are continuous in nature.

Benzol may also be recovered from manufactured-gas operations, and during both World Wars I and II many installations for light-oil recovery were installed in city gas plants. Between wars recovery did not prove economic, and most units were dismantled or allowed to decay through disuse. Recovery in such plants varied from 0.10 to 0.25 gal per 1,000 cu ft. The chief reason for such variation in production economics was that, before World War II, the major use of benzol was as a motor fuel, with price pegged only a few cents per gallon above gasoline. Since the war, less than 20 per cent of the benzol produced at coke plants has been "motor benzol" (less than 6 per cent in 1948); the major portion has been 1° and 2° benzol for chemical use. Before the war "motor benzol" accounted for over 75 per cent of the benzol produced.

The distillation of coal tar from by-product coke-oven operations also yields benzol as one of the distillation products. In general, benzol recovery from this source amounts to about 20 to 30 per cent of that recovered directly in coke-oven operations.

During the past war, the great demand for benzene for cumene manufacture for aviation gasoline and styrene manufacture for synthetic rubber left supplies extremely low, even though many additional recovery facilities were built. Toward the end of the war consideration was being given to enhancing high-grade benzol supplies by the high-temperature cracking of selected petroleum stocks.

A limited amount of motor benzol (2,500,000 bbl in 1944) has been produced for a number of years as a by-product of certain petroleum-cracking operations. Cracking could be carried out in brick regenerative furnaces (for high temperatures) or in conventional cracking equipment. One of the high-temperature cracking processes used for butadiene production during the war produced large quantities of benzol as a by-product. This by-product stream was impure and was used largely for motor gasoline. Other specific possibilities were (1) recracking aromatic distillates, (2) air-injection thermal cracking, (3) virgin-naphtha cracking, and (4) gas-oil steam cracking. If from any of these processes nitration-grade benzene is required, lower yields must be accepted than if a 90 per cent purity is satisfactory. Probably the major difficulties preventing immediate adoption of processes of this type are separation of the aromatic hydrocarbons from other hydrocarbons in the same boiling range and utilization of the large amounts of gas formed during cracking. However, it appears to be only a matter of time until petroleum will replace coal as the major source of benzene, as it did toluene during the war (see *Toluene*). It is possible, on the other hand, that petroleum toluene may be cheaper than benzene and may replace it for many uses.



Location of Crude Light-Oil, Motor Benzene, and Refined Benzene Plants

The percentage of the cost of coke-oven by-product recovery equipment that should be assigned to benzol recovery is difficult to estimate because of wide variations in operating and accounting practices. As mentioned previously (see *Ammonium Sulfate*), the smallest economic unit for complete by-product recovery consists of 2 batteries of 59 coke ovens each. Based on the coking of 11,300 Btu coal, benzene recovery from such a unit would amount to 1,200,000 gal annually. With lower-grade coal, recovery might be as low as 850,000 gal. A complete by-product-recovery coke-oven plant of this capacity costs about $18,000,000.

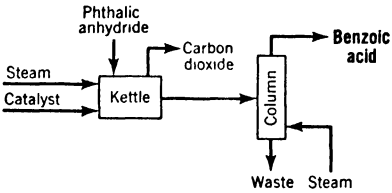
Most of the coke-oven by-product installations are built in conjunction with steel mills and other metallurgical plants. Many of the smaller plants recover light oil only and send it to central plants for separation and refining. The same is true also of most gas plants, which collect "drip oil" and sell it to refiners.

The future supply and demand picture for benzene for chemical manufacture is a mixed one. If blast-furnace operators start using oxygen instead of air, coke production in the industry may drop 50 per cent, with a consequent reduction in by-product benzol supply. Some industries now using benzene may switch to other raw materials, for example, furfural and cyclohexane for nylon (see *Adipic Acid*), and butane for maleic anhydride (see *Maleic Anhydride*). On the other hand, if benzene prices advance sufficiently, the petroleum industry can always initiate production.

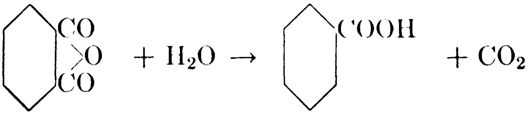
BENZOIC ACID

C_6H_5COOH

From Phthalic Anhydride



Reaction



85% yield

Material Requirements

Basis—1 ton benzoic acid

Phthalic anhydride	2,860 lb
Catalyst	25 lb

Process

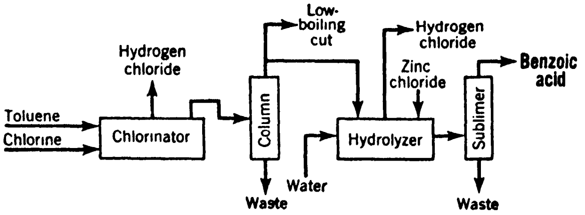
Crude phthalic anhydride is charged into a closed kettle equipped with an efficient agitator. From 2 to 6 per cent by weight of a catalyst, consisting of almost equal parts of chromium and disodium phthalates, is added. The catalyst may be prepared separately or by the direct addition of equivalent amounts of chromium hydroxide and caustic soda to the reaction vessel. The charge is then heated to approximately 200°C, and 2 to 20 parts of steam per hour (based on 100 parts of phthalic anhydride) is introduced below the surface of the mixture. A reflux condenser returns the water, benzoic acid, and phthalic acid to the reaction kettle, while carbon dioxide is vented to the atmosphere. The reaction is allowed to continue until the mixture contains less than 5 per cent phthalic acid. The benzoic acid is then separated from the reaction mixture by distillation with or without the aid of steam. A more complete separation of the benzoic acid from the unreacted phthalic acid may be obtained by adding enough caustic soda to combine chemically with the phthalic acid before distillation. This is commonly carried out in a second steam distillation. The catalyst remaining in the residue may be used again for several batches and eventually may be recovered by dissolving the residue in a solution of soda ash and filtering off the metal precipitate.

Benzoic acid may also be obtained by passing vapors of phthalic anhydride admixed with steam (10 to 50 times the weight of anhydride) over a stationary catalyst maintained at a temperature of 380 to 420°C. A suitable contact mass consists of a mixture of almost equal parts of copper carbonate and calcium hydroxide uniformly coated on pea-size pumice granules.

The resulting reaction product consists essentially of benzoic acid (*ca.* 85 per cent) contaminated with more or less phthalic acid, depending on the loading. A loading of 4 parts of phthalic anhydride per hour per 160 volumes of contact mass at the afore-mentioned temperature is reported to give yields of about 85 per cent of theory based on the phthalic anhydride content of the crude raw material. Small amounts of benzol, diphenyl, benzophenone, and anthraquinone may also be present in the reaction gas.

The benzoic acid may be separated in any suitable manner, for example, by sublimation in the presence of steam or in the presence of vapors of organic solvents for benzoic acid. The hot reaction mixture may be cooled to about 125 to 150°C, and vapors of benzol heated to approximately the same temperature may be bubbled through the mixture. The benzoic acid is almost completely removed, together with any water present. The vapors are cooled to approximately 85°C, at which temperature the benzoic acid condenses; the benzol vapors pass on and can be condensed and re-used after separation from the water.

From Benzotrichloride (Toluene)



Reaction

$$C_6H_5CH_3 + 3Cl_2 \xrightarrow[\text{Heat}]{\text{Light}} C_6H_5CCl_3 + 3HCl$$

$$C_6H_5CCl_3 + 2H_2O \xrightarrow{ZnCl_2} C_6H_5COOH + 3HCl$$

75–80% yield

Material Requirements

Basis—1 ton benzoic acid

Benzotrichloride	3,565 lb
Water (process)	2,500 lb
Catalyst	25 lb

Process

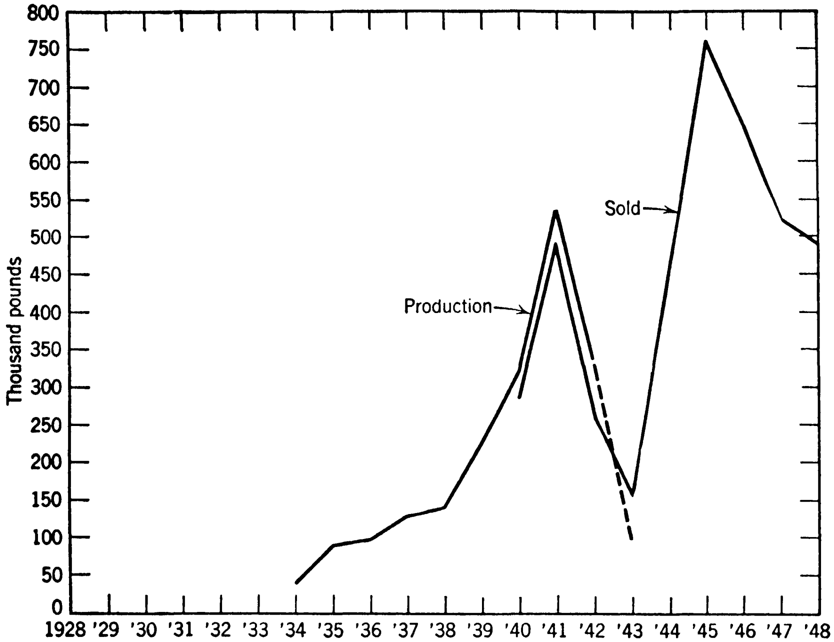
Toluene is chlorinated in the presence of light at 100 to 150°C, until the specific gravity of the solution reaches 1.375 to 1.385 at 20°C, to yield crude benzotrichloride. A small amount of alkali may be added to the reaction product to neutralize any residual hydrogen chloride present. The hydrogen chloride evolved during the reaction is generally absorbed in water to produce hydrochloric acid.

The benzotrichloride may be distilled and then introduced into a suitably lined (such as glass) vessel equipped with an agitator. After the benzotrichloride is heated to about 100°C, approximately 0.7 per cent by weight (based on the charge) of zinc chloride impregnated on pumice is added as a catalyst. Water is then slowly added at a point below the surface of the liquid and is evenly distributed by means of the agitator. Hydrogen chloride is evolved and may be absorbed in water.

The temperature is slowly raised as the reaction proceeds (to prevent solidification), until a temperature of 110 to 115°C is attained. At the completion of the reaction, indicated by the absence of hydrogen chloride evolution, water is added, and the reaction product is allowed to digest for about 0.5 hr with stirring. The temperature is reduced to 90 to 100°C, and more hot water is added to dissolve the zinc chloride and residual hydrochloric acid. The lower acid layer is removed and allowed to solidify; the water layer is cooled, thus precipitating the dissolved benzoic acid, which is removed by filtration, washed with cold water, and added to the solid benzoic acid.

The solid portion contains crude benzoic acid plus varying amounts of water, pumice, and other impurities. It may be converted to sodium benzoate of high quality by dissolving in sodium hydroxide, filtering, and purifying the benzoate solution. The crude acid may be purified to give

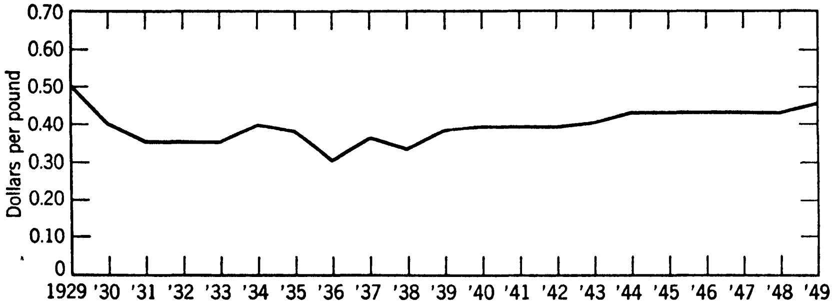
USP benzoic acid by some suitable means such as sublimation or crystallization. A yield of about 90 per cent is realized, based on the weight of benzotrichloride charged.



Production—Benzoic Acid (Technical)

Use Pattern

Food preservative	No breakdown available
Dyestuffs	
Chemicals and pharmaceuticals	
Tobacco curing	
Miscellaneous (resins, perfume bases, toilet preparations, etc.)	



Price—Benzoic Acid (Technical)

Miscellaneous

Properties. White crystalline needles or powder.

Mol. wt.	122.12	M.P.	122.38°C, sublimes at 100°C
Sp. gr.	1.266 15°C/4	B.P.	249.2°C

Slightly soluble in water (0.21 g per 100 ml at 17.5°C, 2.2 g per 100 ml at 75°C). Soluble in alcohol (46.6 g per 100 g at 15°C), ether (66 g per 100 g at 15°C), chloroform (15 g per 100 g at 25°C), benzene (12.2 g per 100 g at 25°C), carbon disulfide, and turpentine.

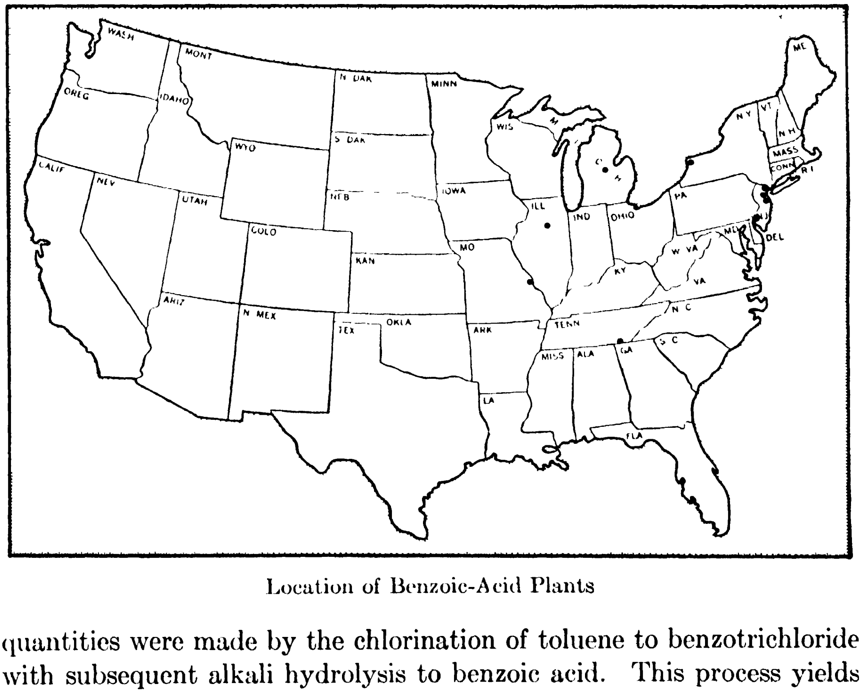
Flash point (closed cup)	250°F
Vapor density (air = 1)	4.21

Grades. Technical (99 per cent) and USP (99.5 per cent).

Containers and Regulations. Barrels (100 to 150 lb), kegs, fiber drums and cartons, and bottles of various smaller sizes. No ICC shipping label is required.

Economic Aspects

Benzoic acid is made chiefly today by the first process described in the foregoing: the decarboxylation of phthalic acid. Previously, large quantities were made by the chlorination of toluene to benzotrichloride with subsequent alkali hydrolysis to benzoic acid. This process yields chlorine-contaminated acid, which is particularly undesirable when



Location of Benzoic-Acid Plants

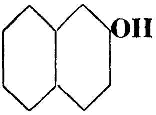
used in conjunction with perfumes and flavoring materials. Some benzoic acid is made as a by-product in the manufacture of benzaldehyde (see *Benzaldehyde*). The catalytic vapor-phase oxidation of toluene yields chlorine-free benzoic acid but cannot compete with decarboxylation, because of difficulties in process control and the high percentage of by-products formed. Some study has been made of a process for making chlorine-free benzoic acid by the aluminum chloride-catalyzed reaction of benzene and phosgene.

Manufacturing plants vary widely in size from very small units up to units with capacities of over 500,000 lb per yr. During World War II, the Germans built an interesting plant at Ludwigshafen in which the hot conversion gases from a phthalic anhydride plant were passed over a zinc oxide–alumina (2-to-1) catalyst for direct decarboxylation of phthalic anhydride to benzoic acid. The plant had a capacity of 60 tons of benzoic acid per month. A yield of 90 per cent based on phthalic anhydride was claimed.

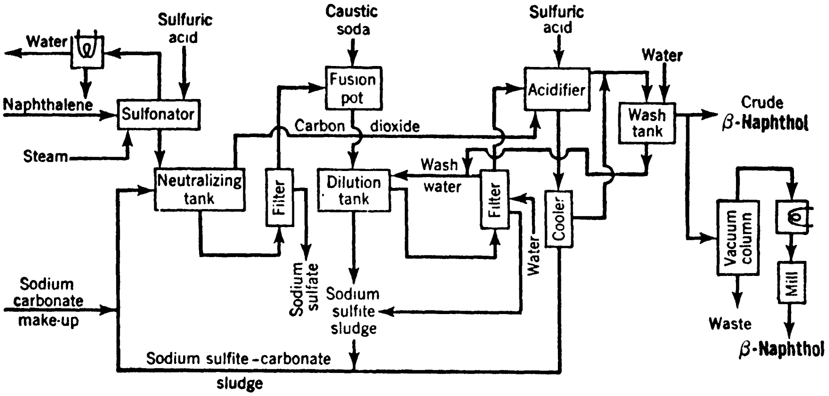
The uses of benzoic acid are fairly well stabilized, and any large increase in use may be expected to be in an entirely new field. Benzyl benzoate can be made from benzoic acid, but benzaldehyde is the preferred raw material (see *Benzaldehyde*).

BETA-NAPHTHOL

(2-NAPHTHOL)



From Naphthalene



Reaction

$$C_{10}H_8 + H_2SO_4 \rightarrow C_{10}H_7SO_3H + H_2O$$

$$2C_{10}H_7SO_3H + Na_2CO_3 \rightarrow 2C_{10}H_7SO_3Na + CO_2 + H_2O$$

$$C_{10}H_7SO_3Na + 2NaOH \rightarrow C_{10}H_7ONa + Na_2SO_3 + H_2O$$

$$2C_{10}H_7ONa + CO_2 + H_2O \rightarrow 2C_{10}H_7OH + Na_2CO_3$$

70–80% yield

Material Requirements

Basis—1 ton β-naphthol

Naphthalene	2,400 lb	Sodium carbonate	1,800 lb
Sulfuric acid (66°Bé)	3,000 lb	Sodium hydroxide	1,700 lb

Process

β-Naphthol is produced by the alkali fusion of sodium naphthalene-β-sulfonate, which in turn is obtained by neutralizing the sulfonation product of naphthalene.

Naphthalene is charged into a sulfonating kettle and melted by heating to about 90°C. With rapid agitation, an almost equal weight of sulfuric acid (66°Bé) is gradually added to the melt, permitting the temperature to rise to 160°C. The sulfonator is maintained at this temperature until all the acid has been added. The charge is then heated at 160 to 165°C for several hours, during which time water and some of the naphthalene distil off. The condenser is kept at 90°C, and the condensed naphthalene is recovered, dried, and re-used.

At the end of the reaction the product contains a mixture of about 85 per cent naphthalene-β-sulfonic acid, and 15 per cent of the alpha isomer. The latter is removed by blowing dry steam through the reaction mixture whereby the naphthalene-α-sulfonic acid is hydrolyzed. The liberated naphthalene is distilled off, recovered, dried, and re-used. A temperature of 160 to 165°C is maintained for the hydrolysis, and about 18 per cent of the original naphthalene is recovered. Of this, approximately 3 per cent is distilled and condensed during the sulfonation, and 15 per cent results from the naphthalene-α-sulfonic-acid hydrolysis.

The sulfonation mixture, contaminated with about 0.1 per cent of the alpha isomer, is discharged into a neutralizing tank where the acid is converted into the sodium salt. This may be accomplished by several methods; the particular process used depends on the individual plant setup. The older method consists of discharging the sulfonation product into water under vigorous agitation (about 4 lb of water per lb of naphthalene originally used). The diluted acid solution is then run into an almost equal weight of salt solution (containing about 1 lb of sodium chloride dissolved in 3 lb of water). Sodium naphthalene-β-sulfonate forms and precipitates on cooling. The sulfonate is filtered, and the filtrate is "salted" again to yield a second crop of crystals. The filter cake, after most of the water is removed, is ready for the alkali fusion.

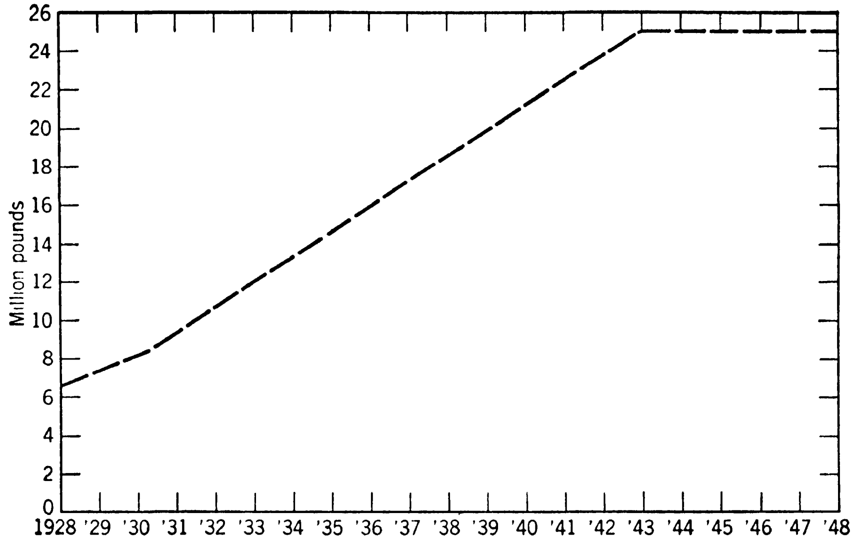
Another method utilizes the sodium sulfite-containing mother liquor from the ensuing β-naphthol precipitation. This liquor is added to the diluted sulfonation mixture, and the resulting sodium naphthalene-β-sulfonate is salted out. The sulfur dioxide liberated is utilized to acidify the β-naphthalate melt. A more detailed discussion of this method is described under *Phenol*, prepared by essentially an analogous process.

A third method consists of treating the dilute naphthalene-β-sulfonic acid solution with the alkali fusion mass from the preceding batch. The following reactions illustrate the procedure:

$$C_{10}H_7SO_3Na + 2NaOH\ \text{(fusion)} \rightarrow C_{10}H_7ONa + Na_2SO_3 + H_2O$$

$$C_{10}H_7ONa + C_{10}H_7SO_3H \rightarrow C_{10}H_7OH + C_{10}H_7SO_3Na$$

A method that competes favorably with the sodium sulfite–sulfur dioxide procedure uses sodium carbonate. The evolved carbon dioxide may be utilized in the ensuing acidification and yet offers none of the disagreeable qualities exhibited by sulfur dioxide. The dilute sulfonation product is neutralized with sodium carbonate. Carbon dioxide is liberated and is piped to the acidifiers. The resulting sodium naphthalene-β-sulfonate–sodium sulfate–sodium carbonate mixture is filtered at the boiling temperature. Most of the sodium sulfate remains on the filter. The filtrate may be cooled to precipitate the β-sulfonate or charged into the fusion kettle *per se*. The fusion pot is charged with fused sodium hydroxide (caustic soda) and heated to 305°C. The sodium naphthalene-β-sulfonate is added to the melt, maintaining the temperature between 295 and 305°C. Generally about 2.8 lb of sulfonate is added per lb of caustic. The fusion is maintained at about 300°C for 6 hr and is then discharged into water or the weak β-naphthol wash water from the previous charge. The resulting hot solution is filtered, and the washed cake is added to the dilution-tank residue (sodium sulfate). The clear mother liquor is charged into the acidifiers.



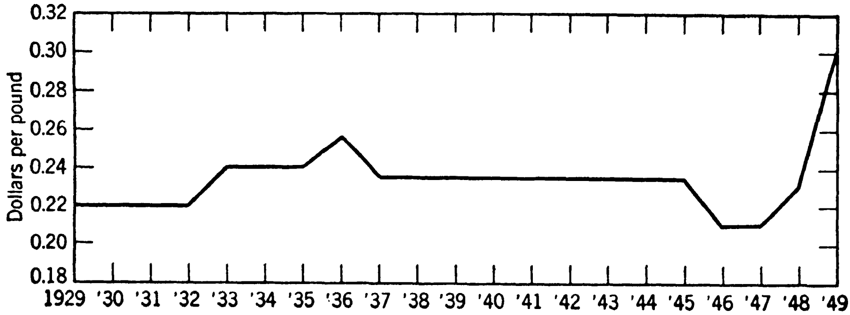
Production—β-Naphthol (Technical—estimated)

Carbon dioxide from the neutralization tank is employed to acidify the diluted caustic fusion melt. A small amount of sulfuric acid is generally added to complete the acidification. Crude β-naphthol separates out as the top layer and is decanted. The bottom layer, consisting of a mixture of sodium sulfite, sodium sulfate, and sodium carbonate, is cooled to recover the 10 per cent β-naphthol contained in it. The solution of salts may be fortified with sodium carbonate and re-used in the neutralization step.

The crude β-naphthol is passed into a tank and thoroughly washed until the water shows a specific gravity of 1.0. These washings may be used to dilute the subsequent fusion melt. The washed product is charged into a vacuum still where the main distillation is carried out at about 28 in. of vacuum and 248°C. Refined β-naphthol is collected in zinc-lined boxes where it solidifies on cooling. The product is broken up and ground to a fine powder. A yield of about 84 per cent is realized based on sodium naphthalene β-sulfonate, and an over-all yield of about 74 per cent is obtained based on the naphthalene used.

Use Pattern

	1947 (est.), per cent
Dyes	65
Rubber	35
	100



Price—β-Naphthol

Miscellaneous

Properties. White, lustrous, bulky leaflets or white powder.

Mol. wt.	144.16	M.P.	123°C
Sp. gr.	1.217 4°C	B.P.	286°C

Soluble in alcohol, ether, benzene, chloroform, and glycerine. Slightly soluble in water (0.1 per cent cold, 1.25 per cent hot).

Flash point (closed cup)	310°F
Vapor density	4.97

Grades. Technical, and USP (resublimed).

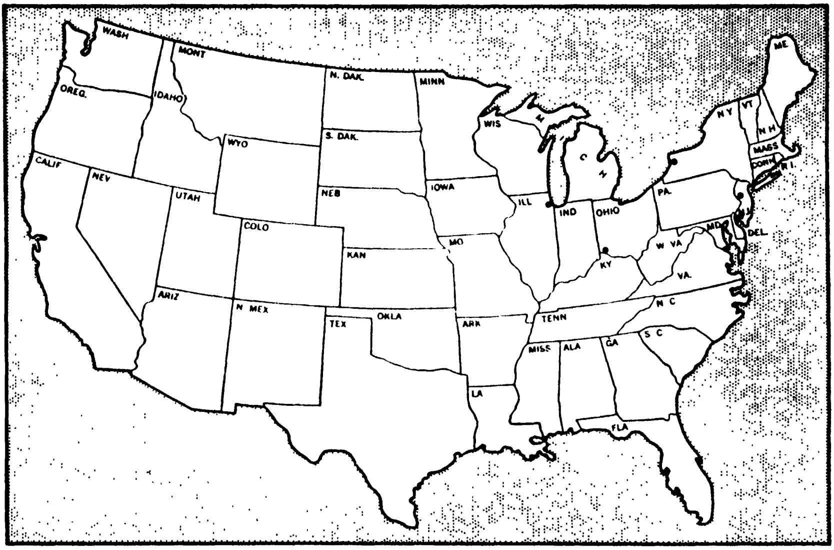
Containers and Regulations. Wooden barrels, cartons, and bottles. No ICC shipping label required.

Economic Aspects

β-Naphthol is one of the chief intermediates in the coal-tar dye industry, and accordingly its production is linked closely to variations in dye manufacture. During World War II, however, large quantities of β-naphthol were required in the manufacture of synthetic-rubber antioxidants. This market remained after the war, and, consequently, supply was still tight in late 1948.

The manufacturing process is similar to the sulfonation process for phenol production but is considerably more difficult because of the production of α- and β-naphthylsulfonic acids, which must be separated by chemical means before alkali fusion. Plants probably vary in size from 1,000,000 to 10,000,000 lb annual capacity. The larger plants require an initial investment of 10 to 12 cents per annual pound.

No drastic process changes are foreseen in the future.



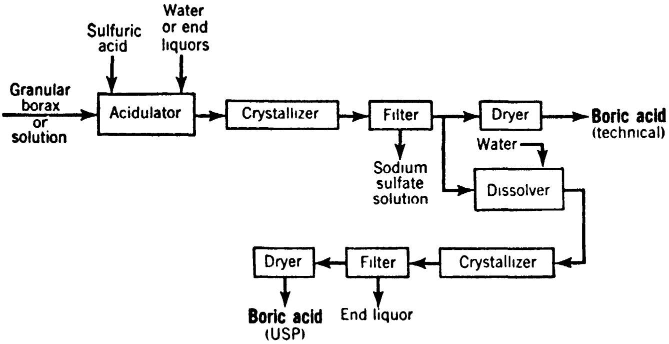
Location of β-Naphthol Plants

BORIC ACID

(BORACIC ACID, ORTHOBORIC ACID)

H_3BO_3

From Borax by Acidulation



Reaction

$$Na_2B_4O_7 \cdot 10H_2O + H_2SO_4 \rightarrow 4H_3BO_3 + Na_2SO_4 + 5H_2O$$

80–90% yield

Material Requirements

Basis—1 ton boric acid

Borax	3,600 lb
Sulfuric acid (66°Bé)	1,260 lb

Process

Boric acid is usually produced by acidifying a saturated solution of borax. It may also be obtained from borate minerals such as rasorite ($Na_2B_4O_7 \cdot 4H_2O$), ulexite ($NaCaB_5O_9 \cdot 8H_2O$), or colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$) by the same method.

Borax ($Na_2B_4O_7 \cdot 10H_2O$), chemically known as sodium tetraborate or pyroborate, is obtained by two processes. One of these makes use of a crude sodium borate called kernite ($Na_2B_4O_7 \cdot H_2O$) or rasorite

($Na_2B_4O_7 \cdot 4H_2O$). Kernite, naturally occurring in Kern county, Calif., lies 350 to 800 ft underground and contains the borate mineral mixed with considerable quantities of clay and shale. The crude ore is mined, crushed, calcined (roasted), and concentrated to remove the clay and shale impurities. The resulting crude borax contains about 45 per cent sodium tetraborate.

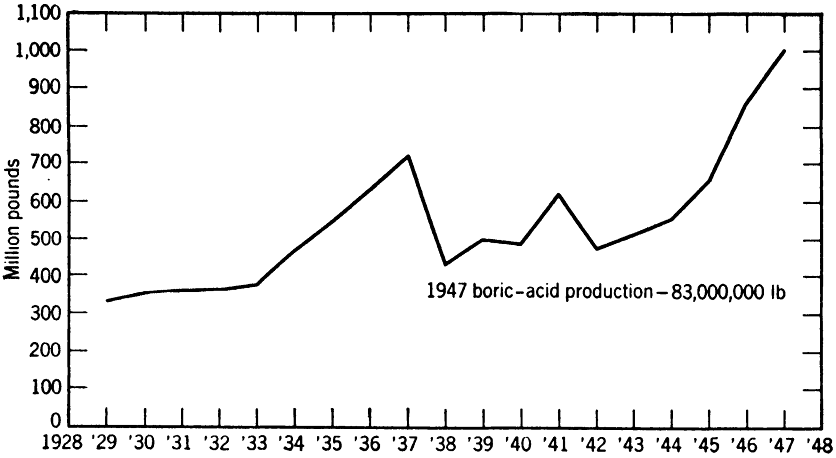
Refined borax is produced by dissolving the crude material in hot water under pressure. The insoluble impurities are filtered off, and the hot saturated solution is either sent to the boric-acid plant or cooled to crystallize the refined product. Borax may also be produced from colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$) by boiling the powdered mineral with sodium carbonate solution for about 3 hr. After filtering, the solution is allowed to crystallize to yield crude borax.

The other process utilizes brine (containing 1 to 2 oz borax per gal) from Searles Lake, Calif., as the raw material. Actually, the borax is obtained as a by-product in the production of potash. The lake is a solid salt bed of very complex composition. A saturated brine solution, containing principally potassium, sodium, chloride, carbonate, borate, and phosphate ions, lies below and fills the interstices between the salt crystals. The brine is pumped from wells at a level about 60 to 70 ft below the surface of the crusty salt deposit. The brine is mixed with end liquors from the process and is concentrated in triple-effect evaporators. After filtering, a saturated solution of borax and potassium chloride is obtained. On rapidly cooling the solution, potassium chloride crystals separate, leaving a saturated solution of borax. The crude borax is then crystallized and separated by continuous rotary filters, and the mother liquor is recycled by mixing with the incoming brine.

The crude borax is dissolved in hot borax mother liquor, filtered, and crystallized again in vacuum crystallizers. The material is centrifuged and dried to yield refined or purified borax.

In the manufacture of boric acid, a hot saturated solution of borax (obtained from the borax-refining plant) or finely granulated borax is charged into an acidifier. Sulfuric or hydrochloric acid, concentrated or dilute, is added until the resulting solution is strongly acid. For example, 3 parts of borax in 12 parts of hot water require about 1 part of concentrated sulfuric acid. The hot solution is run from the acidifier into vacuum crystallizers where it is cooled. Crystalline boric acid forms at a temperature just above that at which sodium sulfate begins to crystallize. Therefore, if sulfuric acid is used, the solution is cooled to the proper temperature, and the crystals of boric acid are removed by filtration. The mother liquor, a saturated solution of sodium sulfate, is cooled further to recover the sulfate salt.

The crude boric acid may be refined by one or more recrystallizations from water to yield purified (USP) boric acid.

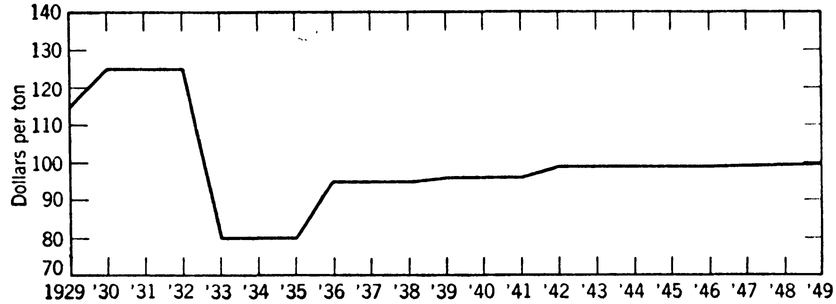


Production—Boron Minerals

Use Pattern

Ceramic glazes
Optical glass
Antiseptic and preservative
Tinning processes
Baking-powder extender
Medicinal (eyewashes, etc.)
Fireproofing agent

No breakdown available



Price—Boric Acid (Technical)

Miscellaneous

Properties. White, translucent, shining, monoclinic or triclinic crystals having a greasy feel. Also white powder.

Mol. wt.	61.84	M.P.	* 185°C, Loses water, decomposes
Sp. gr.	1.435 (15°C)	B.P.	—

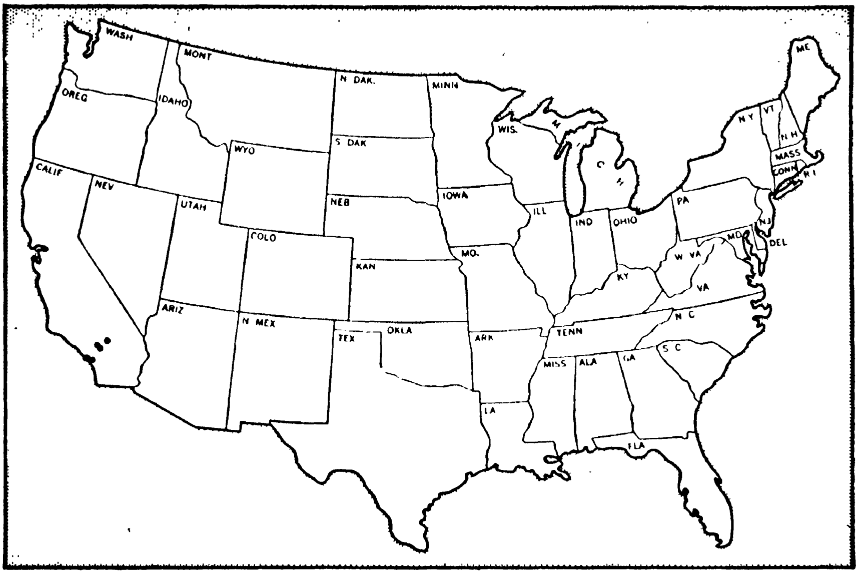
Soluble in water (2.66 g per 100 g at 0°C, 40.2 g per 100 g at 100°C), glycerine (28 g per 100 g at 20°C). Slightly soluble in ether (0.24 g per 100 g at 25°C), and alcohol.

Grades. USP, C.P., and technical (crystals, powder, and impalpable powder).

Containers and Regulations. Barrels, bags, kegs, boxes, cartons, and bottles. No ICC shipping label required.

Economic Aspects

The United States accounts for about 90 per cent of the world's production of boron compounds, most of which are shipped in the form of borax ($Na_2B_4O_7 \cdot 10H_2O$). The chief chemical derivative of borax is boric acid, which is made by the process described previously.



Location of Boric-Acid Plants

Until a few years ago, the bulk of borax production was derived from colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$) by decomposition with soda ash. It is now cheaper to derive borax from lake brines, and over 100,000 tons per year are currently taken from Searles Lake in California, along with a variety of other chemicals. Recently one company has started to mine kernite ($Na_2B_4O_7 \cdot H_2O$) near Kramer, Calif., and is now the world's largest producer of borax.

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* Boric or orthoboric acid (H_3BO_3), when heated to 107°C, is converted into metaboric acid (HBO_2). At 140°C it changes to pyroboric acid ($H_2B_4O_7$), and above 184 to 185°C boric-acid glass (B_2O_3) is formed.

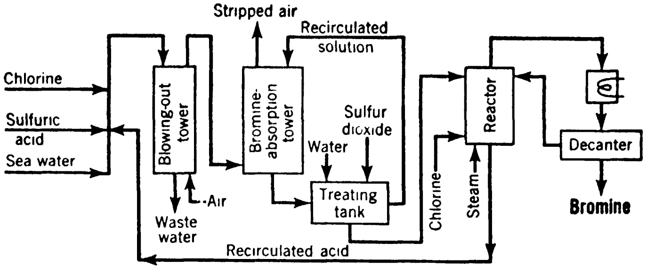
The major portion of boric-acid production is by borax producers themselves, although a small amount of high-grade material is made by secondary producers. A boric-acid plant *per se* is quite simple, and the economic size of plant appears to vary from 10,000 to 30,000 tons per year.

A use pattern for boron compounds is difficult to determine. It is known that larger quantities are being used each year as a minor constituent of mixed fertilizers, although, even here, the greater portion used is an undried boron ore concentrate. During World War II, industrial demand for boron compounds was occasioned largely by their use as a replacement for other scarce materials. Much of this replacement demand has disappeared since the war.

BROMINE

Br_2

From Sea Water



Reaction

$$2NaBr + Cl_2 \rightarrow Br_2 + 2NaCl$$

$$Br_2 + SO_2 + 2H_2O \rightarrow 2HBr + H_2SO_4$$

$$2HBr + Cl_2 \rightarrow Br_2 + 2HCl$$

90–95% yield (recovery)

Material Requirements

Basis—1 ton bromine

Sea water	17,000 ton
Chlorine	900 lb
Sulfuric acid (96%)	5,000 lb
Sulfur dioxide	1,000 lb
Air	Variable

Process

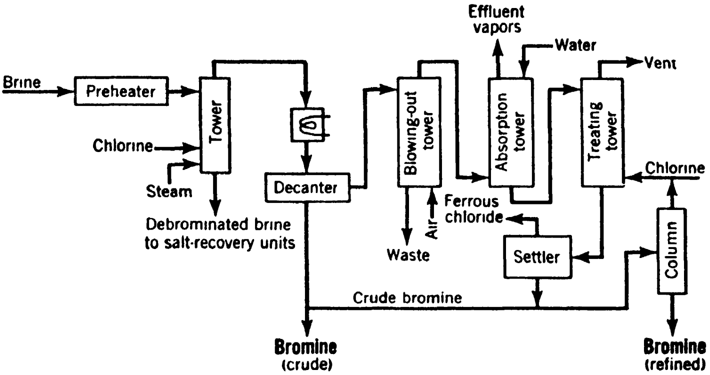
Bromine is recovered from sea water, which contains the element in the form of bromide ions in concentrations of 65 to 70 ppm. The brine is oxidized by chlorine to liberate free bromine, which is vaporized and expelled by a current of air. The bromine is removed from the air stream by sulfurous-acid absorption and freed from the acid solution by the action of chlorine and steam.

Sea water, containing about 3.5 per cent total solids (chiefly the chlorides of sodium, magnesium, and calcium) and 0.007 per cent bromine, is screened to remove debris. The slightly alkaline brine (7.2 *p*H) is allowed to settle and is rescreened before it is pumped through a large rubber-lined pipe to the top of a blowing-out tower. Recovered acid (sulfuric and hydrochloric) from the end of the process is added to the clarified brine near the bottom of the pipe in order to decrease chlorine consumption and obtain a satisfactory recovery of bromine. This residual acid is supplemented with dilute (10 per cent) sulfuric acid so that the *p*H of the brine is reduced to about 3.5. Liquid chlorine is vaporized and added to the acidified brine stream at a point prior to its entry into the blowing-out tower. In the wood-packed tower, the acidified and oxidized sea water is sprayed countercurrent to a voluminous flow of air introduced by a blower at the base of the tower. The air vaporizes and blows out the free bromine from the brine. The debrominated sea water is discharged from the bottom of the tower and is returned to the sea at a point distant from the entrance.

The bromine-containing air stream passes into the bottom of a packed (Raschig rings) absorption tower. Here it is scrubbed by a sulfur dioxide–water solution (sulfurous acid) to absorb the bromine; the stripped air is vented at the top. Part of the bromine reacts with the sulfur dioxide to give sulfuric and hydrobromic acids. The latter absorbs any remaining bromine. The acid liquor flows into a treating tank where it is fortified with sulfur dioxide and water (if necessary). The liquor is recirculated to the top of the absorber and gradually builds up a concentration of hydrobromic acid. The concentrated hydrobromic-acid–bromine solution is continuously withdrawn from the bottom of the treating tank and charged into a reactor. Chlorine is added to the acid solution to liberate the bromine, which is vaporized by steam. The vapors (bromine and water) are condensed and collected in a decanter. The condensate separates into a layer of liquid bromine and an upper aqueous layer saturated with bromine. The upper layer, also containing some hydrobromic acid, is returned to the reactor. The sulfuric- and hydrochloric-acid solution (containing traces of bromine) is discharged from the bottom of the reactor and is returned to the beginning of the process to supply part of the acid required to acidify the entering sea water.

Crude bromine is withdrawn from the bottom of the decanter and is stored, packaged, or sent to ethylene dibromide-producing units. The over-all efficiency of the recovery process is 90 to 95 per cent.

From Natural Brines and Bitterns



Reaction

$$CaBr_2(+ 2NaCl) + Cl_2 \rightarrow Br_2 + CaCl_2(+ 2NaCl)$$

$$Br_2 + Fe \rightarrow FeBr_2$$

$$FeBr_2 + Cl_2 \rightarrow Br_2 + FeCl_2$$

95% yield (recovery)

Material Requirements

Basis—1 ton bromine

Brine	1,000 ton
Chlorine	1,100 lb
Air	Variable

Process

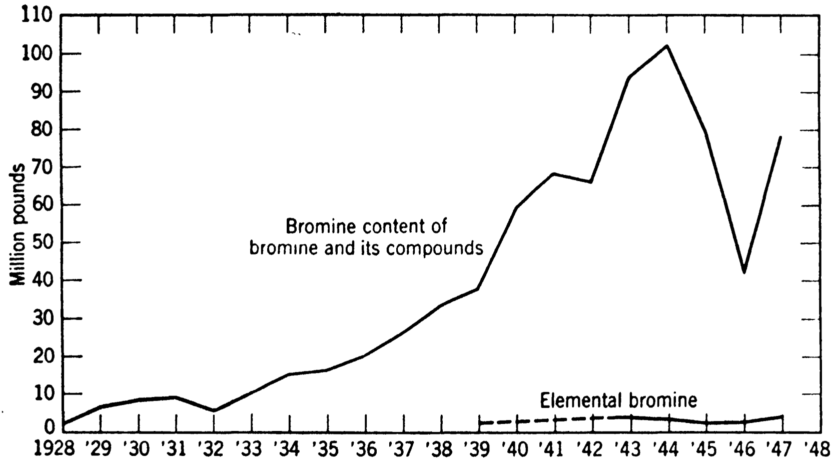
Bromine is recovered from natural brines and bitterns by a method that does not differ basically in principle from the sea-water process. These brines have a much higher bromine content than sea water and, therefore, lend themselves to easier extraction processes. Bromine must be considered a by-product, however, since the prime products of natural brines are the various alkali metal salts (chiefly chlorides). The particular process (or modification) used depends on the nature of the raw material as well as on the type of product desired.

The natural brines of Michigan contain about 1,300 ppm bromine. One such brine contains approximately 26 per cent total solids, consisting chiefly of sodium chloride (14 per cent), calcium chloride (9 per cent), and magnesium chloride (3 per cent), together with about 0.13 per cent bromine. The brine is preheated to just below the boiling point and charged into a corrosion-resistant tower where it is reacted with chlorine (sometimes in the presence of sulfuric acid). The reaction may be carried out, using a tower of special design containing a number of compartments. Chlorine gas is introduced near the base of the tower and oxidizes the hot descending brine; good mixing and distribution are obtained in each compartment. The liberated bromine is vaporized and blown out of solution by steam. The debrominated brine is discharged through the bottom of the tower and sent to salt-recovery units. See *Calcium Chloride.*

The vapors, consisting of bromine, a little chlorine, and steam, leaving the top of the tower, are condensed and passed into a decanter. A lower layer of crude bromine and an upper layer of bromine water separate. The latter may be returned to the tower, or the bromine in it may be recovered by blowing with air. The resulting vapor mixture is passed through an absorbing tower filled with wet iron filings to form ferrous bromide. The concentrated bromide solution is treated with chlorine to liberate bromine, which is only slightly soluble in the simultaneously formed ferrous chloride. The crude bromine settles to the bottom of the chamber from where it is withdrawn.

A modification of this process consists essentially of oxidizing the brine with chlorine to liberate the bromine. The free bromine is blown out of solution by air and is absorbed from the air by an alkaline carbonate solution (sodium carbonate), from which it is subsequently recovered by acid treatment.

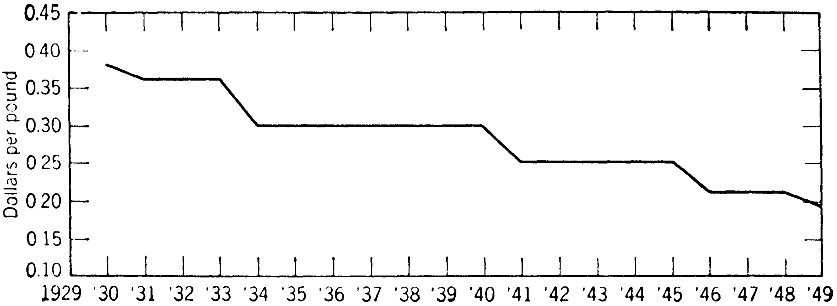
The crude bromine from the decanter and settling chamber may be purified by distillation, which removes most of the residual chlorine. The recovery yield is about 95 per cent.



Production—Bromine

Use Pattern

	Per cent
Ethylene dibromide	90
Miscellaneous (chiefly inorganic bromides)	10
	100



Price—Bromine

Miscellaneous

Properties. Dark reddish-brown liquid with irritating fumes, which burn the skin on contact.

Mol. wt.	159.83	M.P.	−7.2°C
Sp. gr.	3.119 (20°C)	B.P.	58.80°C
	Vapor density 7.59 gpl (20°C)		

Soluble in water (4.22 g per 100 ml at 0°C, 3.13 g per 100 ml at 30°C), alcohol, ether, alkalies, and carbon bisulfide.

Grades. Technical, C.P., USP, and N.F.

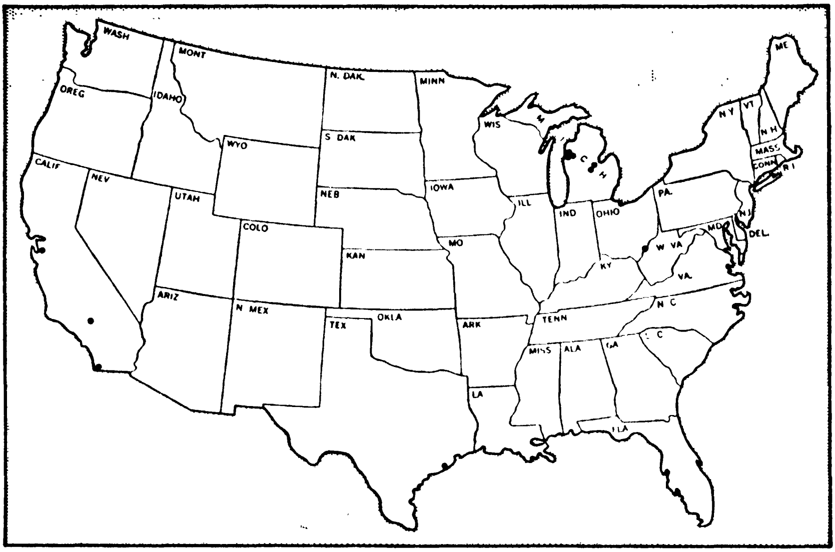
Containers and Regulations. Tank cars, lead-lined steel, nickel, and Monel drums, earthenware bottles, and glass bottles. The fumes and vapors of bromine are poisonous. A fire may be produced when the material contacts organic matter such as sawdust or excelsior. White ICC shipping label required.

Economic Aspects

Until 1934 American bromine producers recovered the element from salt brines, some of which contained as much as 1,300 ppm bromine in the form of bromides. Greatly increased requirements for ethylene bromide, a constituent of "Ethyl Fluid," led to the development of bromine recovery from sea water in which it is present only to 65 to 70 ppm. The single plant using this process is said to have an annual capacity of 10,000 tons of bromine. Most of the bromine is converted to ethylene dibromide at the point of manufacture and shipped as such.

Bromine, however, is only one of the products removed by producers from salt brines, since common salt (NaCl) and magnesium chloride are usually the chief products. Besides liberation from the brines by the use of chlorine, the usual process, it is also possible to liberate the element by electrolysis of a bromide solution. The process has never been used, however, except to a small extent.

The future of bromine production is intimately related to the demand for "Ethyl Fluid," the well-known antiknock formulation. Many attempts have been made to develop either substitute or superior antiknocks. None of these efforts have been successful, but the possibility exists and could affect bromine production markedly.



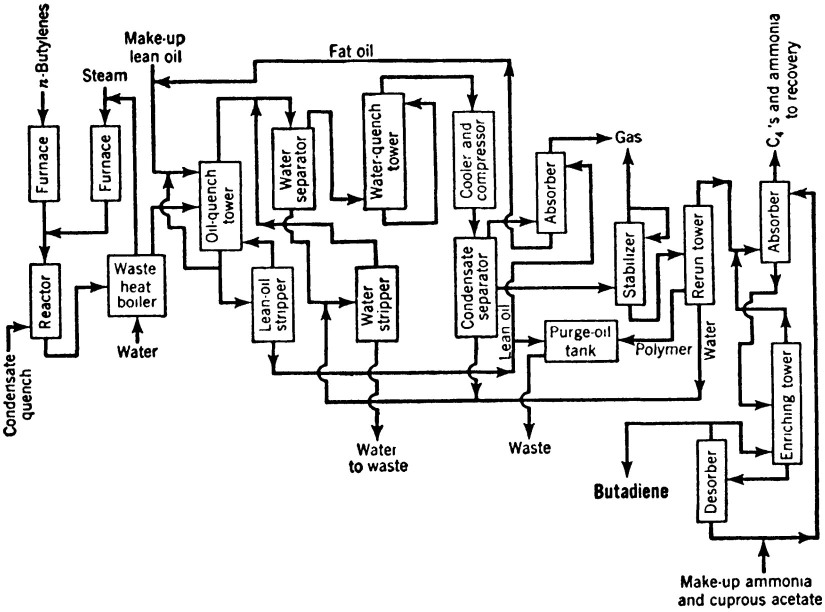
Location of Bromine Plants

BUTADIENE

(BUTADIENE-1,3)

$CH_2{=}CHCH{=}CH_2$

From Butylenes by Dehydrogenation



Reaction

$$n\text{-}C_4H_8 \rightarrow CH_2{=}CHCH{=}CH_2 + H_2$$

65–75% yield

(0.65–0.75 lb butadiene per lb *n*-butylenes consumed)

Material Requirements (Major)

Basis—1 ton butadiene (98%)

Butylenes 2,700–3,000 lb

Process

Butadiene is produced from petroleum chiefly by the catalytic dehydrogenation of normal butylenes. To minimize carbon formation, the reaction is carried out at low partial pressures, usually attained by the use of an inert gas as a diluent. The crude butadiene, obtained in yields of 25 to 30 per cent per pass, is purified by extraction and distillation to give the commercial 98 to 99 per cent product.

Normal butylenes (butenes) are produced by catalytic cracking processes or are obtained from refinery butene-containing fractions. Crude gases are treated by extractive distillation using furfural to remove normal and isobutanes, isobutylene, pentanes and other impurities so that essentially *n*-butylenes (butene-1 and butene-2) are available as raw-material feed. The butylenes are preheated in heat exchangers and then heated in a furnace to about 1,100°F. Steam, used as a heat-carrying diluent, is superheated to approximately 1,300°F. The two streams pass through jet-type mixers located directly above the reactor. Here steam and normal butylenes are mixed in a ratio of 15–20 to 1, depending on the purity of the feed (70 to 80 per cent normal butylenes in feed is common). About a 25-lb pressure drop is taken across the mixing nozzles to insure adequate mixing energy.

The dehydrogenation reactors (steel-alloy) are about 16 ft in diameter and contain a single fixed bed of catalyst pellets ($^3/_{16}$ in. in diameter and $\frac{1}{4}$ in. long) varying in depth from 42 to 60 in. and supported on steel-alloy (18-8) sectional grates. The operating-temperature range is 1,150 to 1,250°F (50 to 75°F temperature drop through catalyst bed) at a superficial reactant residence time of about 0.2 sec (space velocity of about 400 volumes per hour per volume of catalyst). The dehydrogenation reaction is highly endothermic, requiring an external heat source of about 725 Btu per lb of butylenes converted. The conversion per pass over the catalyst, known as "Catalyst 1707" is 25 to 30 per cent. A minimum temperature of 1,100 to 1,150°F is required for reasonable butylene conversion, but to avoid thermal cracking of the butylenes in the heaters it is necessary to operate below 1,300°F. A cyclic operation using two reactors is employed to maintain activity of the catalyst. Regeneration is accomplished by shutting off the butylene feed and allowing the steam to remove carbon from the catalyst by the water-gas reaction. Under operating conditions, about a 5 per cent shrinkage of the catalyst takes place; the life of the catalyst (72.4 MgO, 18.4 Fe_2O_3, 4.6 CuO, 4.6 K_2O) is 2 to 3 months under normal conditions.

The reaction gases are quenched to about 950°F by means of a stream of condensate as they leave the catalyst bed. The hot effluent from the reactor is cooled in a waste heat boiler and then cooled further in a series of quench towers. The condensate obtained, containing the bulk of the C_4 hydrocarbons, is charged into a fractionating column, where it is stabilized by separation of a light overhead stream. The stabilized condensate leaving the bottom of the column is passed into a rerun tower, where polymerized material is removed from the bottom, and crude butadiene along with other C_4 hydrocarbons is condensed as overhead product. This mixture is run to purification units.

The noncondensable vapors in the cooled effluent condensate are removed by a separator, which allows the vapors to pass into an absorber. Here the C_4 hydrocarbons are recovered by lean oil from the effluent quench system. This oil is circulated in a closed system and is maintained in satisfactory condition by a small make-up feed stream and a lean-oil stripper, which continuously eliminates a small bottoms stream. The noncondensable vapors from the absorber, consisting mostly of hydrogen, are passed to storage for fuel gas. Water vapors in the reactor effluent are condensed, separated, and stripped of volatile hydrocarbons before being discharged.

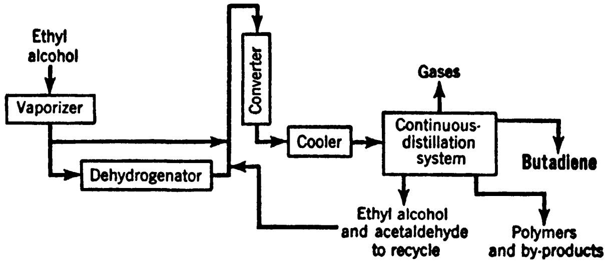
Crude butadiene from the rerun tower may be purified in several ways, such as absorption with cuprous salt solution or extractive distillation with furfural. In the first method, the crude butadiene is passed (in either vapor or liquid state) into the bottom of a packed absorption tower, where it meets a solution of ammoniacal cuprous acetate. The butadiene and small quantities of other unsaturated hydrocarbons (especially butylenes) are dissolved in the solution. This then passes into an enrichment tower, where unsaturated hydrocarbons other than butadiene are stripped from the solution by countercurrent passage of purified butadiene. The enriched butadiene is then passed into a desorption tower for separation from the solution, which is recycled after the addition of make-up ammonia. The butadiene obtained is distilled, compressed, and liquefied to yield product of 98 to 99 per cent butadiene. Ammonia is recovered from the product butadiene in the distillation step and from the C_4 raffinate for recycle in substantially anhydrous form. The C_4 hydrocarbons are returned for re-use.

Crude butadiene of 40 to 50 per cent purity is also separated from butanes and butylenes by extractive distillation, using furfural or by azeotropic distillation with ammonia.

Production of butadiene from butane is really a two-step operation, involving first the dehydrogenation to normal butylenes. Hydrogen and other reaction gases are separated from the normal butylenes, which are then treated in a manner similar to the afore-mentioned description.

In the so-called "quick" program used during the war, butadiene was recovered from reaction gases resulting from the severe thermal cracking of naphtha and similar petroleum fractions. Yields were small (about 2.5 to 5 per cent).

From Ethyl Alcohol



Reaction

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2$$

$$CH_3CH_2OH + CH_3CHO \rightarrow CH_2{=}CHCH{=}CH_2 + 2H_2O$$

70% yield

Material Requirements

Basis—1 ton butadiene

Ethyl alcohol (95%)	800-850 gal

Process

Production of butadiene from ethyl alcohol is a two-step process involving dehydrogenation to acetaldehyde, followed by a catalytic reaction between the aldehyde and excess alcohol. The crude material is separated from the reaction products and purified to 98 to 99 per cent butadiene.

Ethyl alcohol (92 to 95 per cent) is vaporized and passed over a suitable dehydrogenation catalyst such as copper to produce acetaldehyde (for details see *Acetaldehyde*). The aldehyde, obtained in about a 92 per cent yield, is then mixed with an excess of aqueous ethyl alcohol so that a molar ratio of from 2.75 to 3 parts alcohol to 1 part acetaldehyde results. At essentially atmospheric pressure the feed mixture is passed over a tantala–silica catalyst (about 2 per cent tantalum pentoxide on silica gel). The temperature is 325 to 350°C, and the feed rate is 0.4 to 0.5 volumes of liquid feed per volume of catalyst per hour. The yield of butadiene per pass is 28 to 30 per cent based on the two reactants.

The converters consist of numerous steel tubes, about 3 in. in diameter by 20 ft long, containing 3- to 10-mesh catalyst and encased in a tubular boiler. The heat for the endothermic reaction is furnished through a temperature-regulating bath of Dowtherm, which surrounds the tubes.

After the catalyst has been used about 120 hr, it loses activity, owing to carbon deposition. Regeneration takes place by passing air over the catalyst *in situ* at about 400°C.

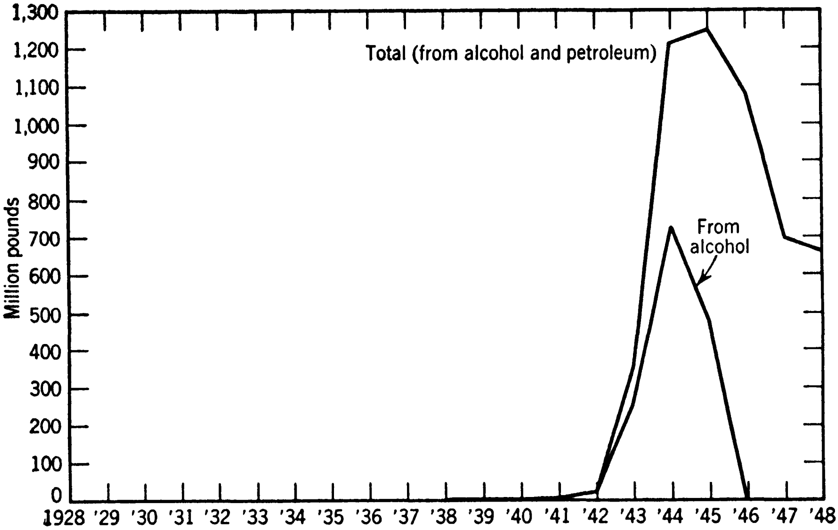
The reaction gases from the converter contain unreacted ethyl alcohol and acetaldehyde, water, and numerous by-products. Of the latter, the major ones include ethyl ether, ethyl acetate, ethylene, hexenes and hexadienes, pentenes and pentadienes, acetic acid, and butanol. After the reaction gases are cooled in heat exchangers, they are passed to a series of columns. Here the butadiene is separated continuously from the lower- and higher-boiling impurities. Several of the by-products such as ethylene, butene, ethyl ether, ethyl acetate, and butanol are recovered. Unreacted ethyl alcohol and acetaldehyde are recycled to the converters. Such by-products as ethyl acetate may also be returned for utilization. Based on the amount of ethyl alcohol consumed, the yield is about 68 mole per cent. Slightly higher yields and conversions per pass may be realized by injecting an auxiliary feed, rich in acetaldehyde, into the middle of the catalyst bed and adding an auxiliary ethyl alcohol stream below the midpoint of the catalyst section.

Other processes, depending on ethyl alcohol as the starting material, have been investigated on a pilot-plant scale. These include the reaction between ethanol and crotonaldehyde (now recognized to be the intermediate in the previously described process) and a more direct conversion of ethyl alcohol into butadiene over a catalyst containing dehydrogenating components.

From Butylene Glycol

Butadiene may also be produced from butylene glycol derived from grain fermentation. Starch is acid-hydrolyzed, and the hydrolyzate is fermented with *Aerobacter aerogenes* to produce meso-2,3-butylene glycol. Approximately 14.5 lb of glycol is obtained per bu (56 lb) of wheat. About 95 per cent of the butylene glycol is recovered from the fermented mash by steam distillation. The glycol is esterified (about 97 per cent yield) to yield 2,3-butylene glycol diacetate, which is then pyrolyzed to 1,3-butadiene. A yield of about 88 per cent is realized on this step to give a total yield of about 7 lb of butadiene per bu grain. Acetic acid is recovered for re-use in the esterification, whereas ethyl alcohol, methyl ethyl ketone, and dry grain are recovered as by-products.

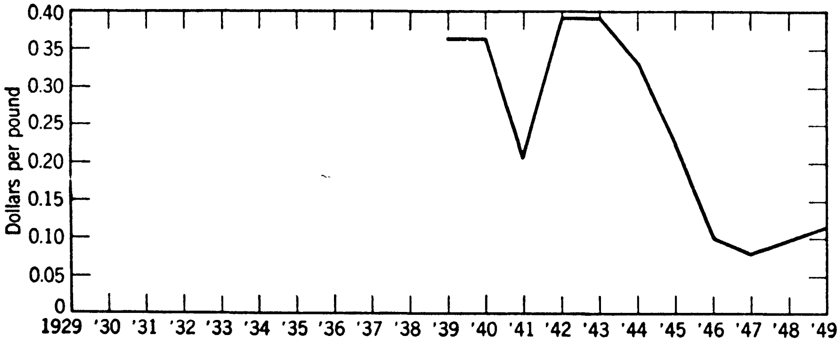
This process was developed during the war but does not appear competitive with the petroleum and alcohol processes except in periods of emergency.



Production—Butadiene

Use Pattern

	1947 (est.), per cent
Synthetic elastomers	100



Price—Butadiene

Miscellaneous

Properties. Colorless, odorless, flammable gas at normal temperatures which may easily be condensed to a liquid.

Mol. wt.	54.09	M.P.	−108.9°C
Sp. gr.	9.621 20°C/4	B.P.	−4.41°C

Soluble in alcohol and ether. Insoluble in water.

Flash point (closed cup)	Gas
Vapor density (air = 1)	1.87
Explosive limits (% by volume in air)	Lower 2.0 Upper 11.5

Grades. Technical.

Containers and Regulations. Pressure tank cars and cylinders. Red ICC shipping label required.

Economic Aspects

The future of butadiene production is intimately related to the future of synthetic rubber. A small amount was used before World War II in the manufacture of synthetic elastomers and in organic-chemical synthesis (see *Maleic Anhydride*), but large-scale production was warborne and destined entirely for synthetic-rubber production, principally GR-S (Buna S). One long ton of GR-S required 1,610 lb butadiene. In the postwar economy, butadiene production depends not only on the amount of competition to be derived from natural rubber but also on the competition of other synthetic elastomers with GR-S. On the other hand, availability of a cheap hydrocarbon with a highly reactive double bond, such as exists in butadiene, may lead to wide use in the production of various synthetic organic chemicals (see *Adipic Acid*).

The competitive situation between natural and synthetic rubber is largely political, insofar as politics creates false economic conditions. Nevertheless, the consensus of experts is that synthetic elastomers are here to stay. Butadiene is used largely in the Buna-type rubbers and to a smaller extent in the manufacture of butyl rubber. These synthetic elastomers compete with the nonbutadiene elastomers, neoprene, Thiokol, and others, but indications are that butadiene will remain the principal constituent of general-purpose synthetic rubbers for many years. There is always the possibility that other dienes such as hexadiene may be found superior to butadiene, but the actual presence of large butadiene capacity will delay substitution unless tremendous differences in product quality are attained. This appears unlikely.

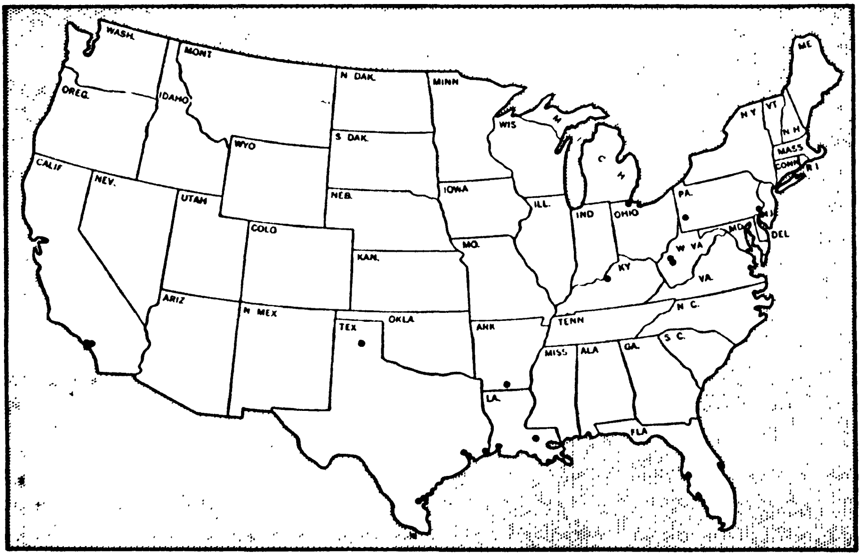
The chief competition between butadiene manufacturing processes is based on the raw material used: ethyl alcohol versus petroleum. This situation is again partly political, because of the interest of political farm groups in an additional industrial outlet for grain. Even in the alcohol process, however, the ethyl alcohol can be obtained more cheaply from petroleum than from grain. So, all in all, it appears that, in a strictly economic sense, butadiene directly from petroleum is cheaper than butadiene from nonpetroleum sources. There is, of course, the long-time possibility that near-exhaustion of petroleum reserves may make annually renewable raw materials more attractive. In this case, coal as a raw material may enter the picture, via either the Fischer–Tropsch process, or through acetylene to acetaldehyde and thence to butadiene. German synthetic rubber produced during World War II was derived from the last-named process.

Competition also exists among various processes based on alcohol and among various methods of obtaining butadiene from petroleum. Both are in a state of flux, and it is difficult to say at this time whether or not the best process in each case has been chosen or even developed. Many believe that the Government should have chosen the aldol process during World War II as the best of the alcohol processes. The place of the butylene glycol fermentation process can hardly be determined until more process development work has been done.

Alcohol butadiene plants during the war were built in units of 20,000 annual tons rated capacity. Two plants had four units each, and another three. Actual production figures, however, indicated that unit capacities were actually 35,000 annual tons. Plant investment cost per annual ton is approximately $300.

Most of the petroleum butadiene plants have rated capacities between 15,000 and 100,000 tons per year but can produce about 40 per cent above rated capacity. Average investment requirements per annual ton for plants of this type are estimated as: $425 from butylene, $550 from naphtha and gas oil, $650 from butane.

The cost of a plant based on fermentation butylene glycol is estimated as $625 per annual ton of butadiene.

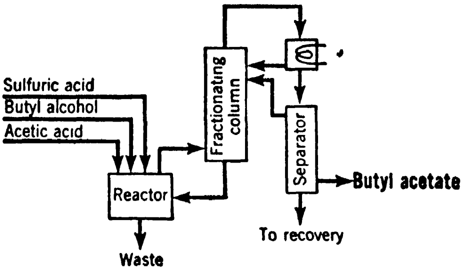


Location of Butadiene Plants

BUTYL ACETATE

$CH_3COOC_4H_9$

From Butyl Alcohol and Acetic Acid by Esterification



Reaction

$$C_4H_9OH + CH_3COOH \xrightarrow{H_2SO_4} CH_3COOC_4H_9 + H_2O$$

95% yield

Material Requirements

Basis—1 ton butyl acetate

Butyl alcohol (normal)	1,425 lb
Acetic acid (glacial)	1,100 lb
Sulfuric acid (66°Bé)	2–8 lb

Process

Acetic acid and *n*-butyl alcohol (10 per cent excess) are charged into a batch still. About 0.1 per cent sulfuric acid (66°Bé) is added as catalyst. The acetic acid should be free from other acids, but its water content is not critical; 80 per cent to glacial acetic acid is most commonly used. The amount of water present determines the length of distillation and limits the capacity of the equipment. The butyl alcohol should contain a minimum of other alcohols or isomers.

The still is heated under total reflux by jacketed steam until the head temperature of the distilling column becomes constant (about 89°C). After this equilibrium has been reached, the distillate is withdrawn from the column as rapidly as possible without raising the head temperature.

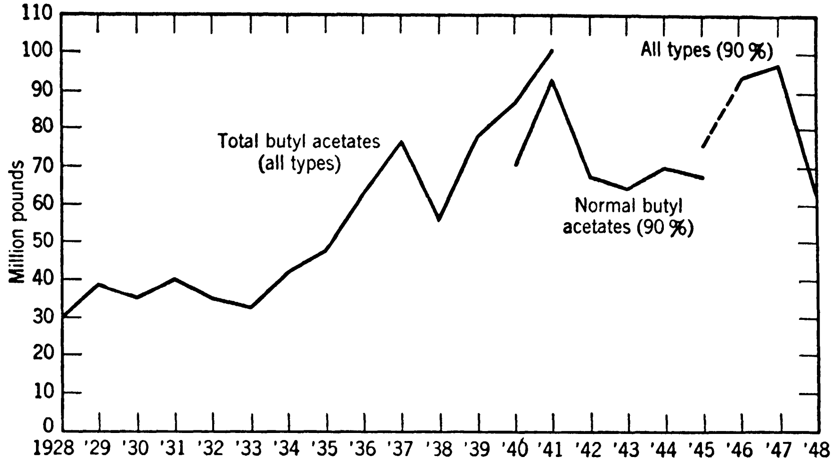
The vapor mixture (approximating the ternary azeotrope; 35.3 per cent *n*-butyl acetate, 27.4 per cent *n*-butyl alcohol, and 37.3 per cent water, B.P. 89.4°C) is condensed and sent to an automatic separator. Here two layers are formed. The top layer, constituting about 75 per cent of the distillate, contains approximately 81 per cent ester, 13 per cent alcohol, and 6 per cent water. This "oily" layer is continuously returned to the distilling column. The lower layer (about 25 per cent of the distillate) contains approximately 1 per cent ester, 3 per cent alcohol, and 96 per cent water. Either this aqueous layer is run to waste, or the alcohol and ester are recovered by distillation, depending on the economics involved.

Toward the end of the distillation, the amount of water coming over greatly decreases, and the head temperature rises. The reflux ratio is increased until no more water is present in the distillate, indicating the completion of the esterification. Generally, the residual acid is neutralized with alkali to minimize decomposition in subsequent operations.

The distillation is continued, and the binary azeotrope (53 per cent ester and 47 per cent alcohol, B.P. 117.2°C) is next obtained. After the alcohol has been exhausted, pure *n*-butyl acetate (B.P. 126.2°C) comes over and is collected. The alcohol and ester fraction may be blended or added to the next batch. Technical (90 to 92 per cent) butyl acetate is obtained at the beginning of the last fraction. Pure (99 per cent) butyl acetate may be obtained in the middle of the last fraction. The over-all yield of *n*-butyl acetate based on the acetic acid charged averages about 95 per cent.

The other acetates of butyl alcohol (*sec*-butyl acetate, isobutyl acetate, and *tert*-butyl acetate) may be prepared in a similar manner, using the corresponding butyl alcohol as raw material. Certain modifications must be made after taking into account both the boiling points of the various esters and the composition of the corresponding azeotropes. For example, isobutyl alcohol, isobutyl acetate, and water form a ternary azeotrope which boils at 86.8°C and contains 23.1 per cent alcohol, 46.5 per cent ester, and 30.4 per cent water. On removal of the water, a binary azeotrope results (containing 92 per cent alcohol and 8 per cent ester), which has a boiling point of 107.6°C. The isobutyl acetate may then be distilled at 118°C to yield a relatively pure ester. The manufacture of this acetate is very similar to that described for *n*-butyl acetate.

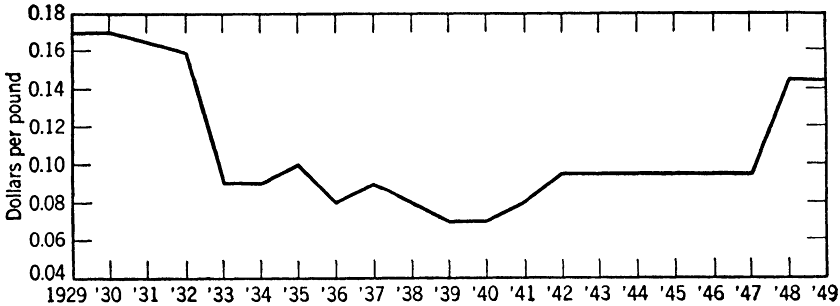
The esterification of acetic acid with *sec*-butyl alcohol proceeds moderately well. However, the reaction between *tert*-butyl alcohol and acetic acid is very sluggish and incomplete. The order of reactivity in the esterification of acetic acid is: Primary butyl alcohols > *sec*-butyl alcohol > *tert*-butyl alcohol.



Production—Butyl Acetate

Use Pattern

	Per cent
Protective coatings	95
Miscellaneous	5
	100



Price—Butyl Acetate (Generally, lowest price for any type)

Miscellaneous

Properties. *n-Butyl Acetate* ($CH_3COOCH_2CH_2CH_2CH_3$). Colorless liquid with a fruity odor.

Mol. wt.	116.16	M.P.	−76.8°C
Sp. gr.	0.882 (20°C)	B.P.	126.5°C

Weight per gallon 7.29 lb (20°C)

Soluble in alcohol and ether in all proportions at room temperature.

Soluble in most hydrocarbons. Slightly soluble in water (0.7 g per 100 g at room temperature).

Flash point (closed cup)	72°F
Ignition temperature	790°F
Vapor density (air = 1)	4.00
Explosive limits (% by volume in air)	Lower 1.7 Upper 15

Isobutyl Acetate [$CH_3COOCH_2CH(CH_3)_2$]. Colorless liquid with a fruitlike odor.

Mol. wt.	116.16	M.P.	−98.9°C
Sp. gr.	0.871 20°C/4	B.P.	118°C

Weight per gallon 7.26 lb

Soluble in alcohol and ether in all proportions. Slightly soluble in water (0.6 per cent) at 25°C.

Flash point (closed cup)	64°F
Vapor density (air = 1)	4.00

sec-Butyl Acetate [$CH_3COOCH(CH_3)CH_2CH_3$]. Colorless liquid with a mild odor.

Mol. wt.	116.16	M.P.	—
Sp. gr.	0.865 25°C/4	B.P.	112–113°C

Weight per gallon 7.21 lb

Soluble in alcohol and ether in all proportions at room temperature. Insoluble in water.

Flash point (closed cup)	66°F
Vapor density (air = 1)	4.00

tert-Butyl Acetate [$CH_3COOC(CH_3)_3$]. Colorless liquid.

Mol. wt.	116.16	M.P.	—
Sp. gr.	0.896 (20°C)	B.P.	97°C

Weight per gallon 7.46 lb

Soluble in alcohol and ether. Insoluble in water.

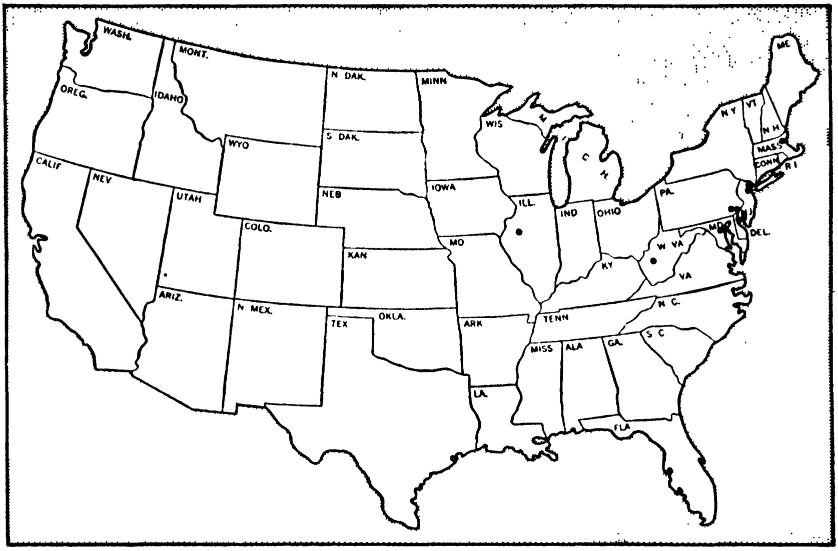
Grades. Technical, *n*-butyl acetate (90 to 92 per cent), *sec*-butyl acetate (85 to 88 per cent); pure (98 to 99 per cent).

Containers and Regulations. Tank cars, drum cars, compartment tanks, steel drums, cans, and bottles. Red ICC shipping label required.

Economic Aspects

The bulk of butyl acetate production is used in the protective-coatings industry as a solvent and thinner. It is, by far, the most important lacquer solvent in the medium-boiling range.

Essentially the same type of plant described for the manufacture of amyl acetate may be used for making the butyl ester. The latter, of course, is the more important of the two esters on the basis of production volume. This volume will probably continue to be guided by requirements for protective coatings.



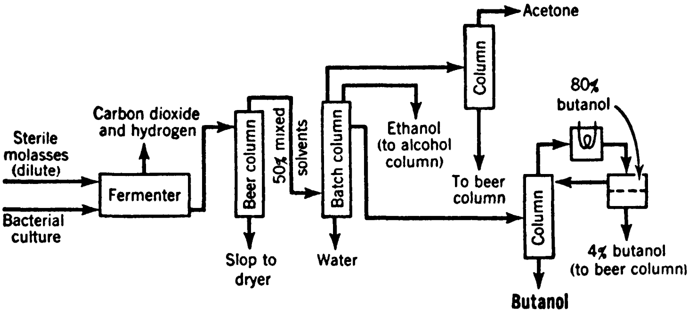
Location of Butyl Acetate Plants

BUTYL ALCOHOL

(BUTANOL)

$CH_3CH_2CH_2CH_2OH$

From Carbohydrates by Fermentation



Reaction

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_x} \xrightarrow{H_2O} \underset{\text{Glucose}}{C_6H_{12}O_6} \rightarrow$$

$$CH_3COCH_3 + CH_3CH_2CH_2CH_2OH + C_2H_5OH + CO_2 + H_2$$

Yield

$$1\text{ gal molasses (6–6.6 lb sugar)} = \begin{cases} 1.45\text{–}1.65\text{ lb butanol} \\ 0.4\text{–}0.65\text{ lb acetone} \\ 0.07\text{–}0.1\text{ lb ethyl alcohol} \\ \text{plus } CO_2 \text{ and } H_2 \end{cases}$$

$$1\text{ bu corn (33 lb starch)} = \begin{cases} 6\text{–}8\text{ lb butanol} \\ 3\text{–}4\text{ lb acetone} \\ 1\text{–}1\tfrac{1}{2}\text{ lb ethyl alcohol} \\ 15\text{–}16\text{ lb—}60\%\ CO_2,\ 40\%\ H_2 \end{cases}$$

Material Requirements

Basis—1 ton butanol

Molasses	1,300 gal
Water	17,500 lb
Nutrients	7 lb

Process

Butyl alcohol (butanol), acetone, and ethyl alcohol are produced by the selective bacterial fermentation of carbohydrate-containing materials such as molasses and grain. The process is described in full under *Acetone.*

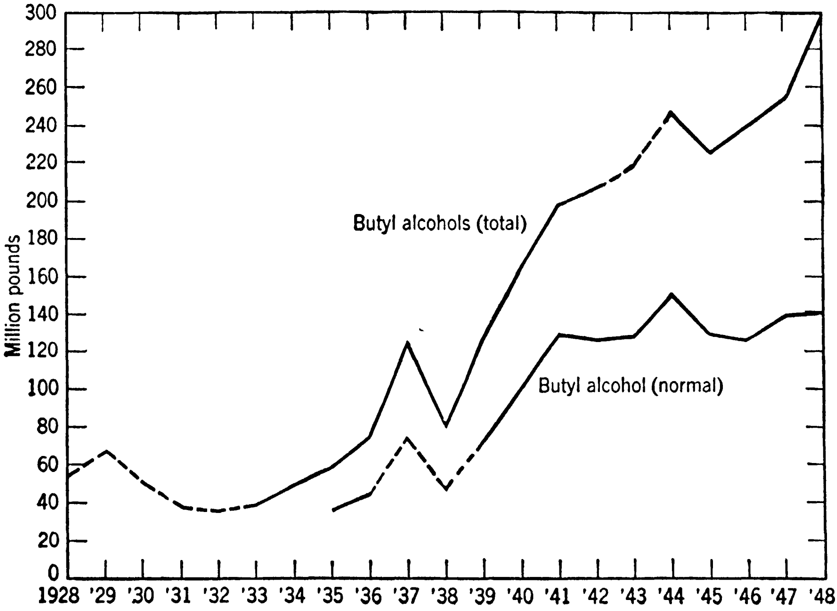
From Crotonaldehyde

Normal butyl alcohol is produced synthetically by the condensation of acetaldehyde to form aldol, which is then dehydrated to crotonaldehyde. The latter is hydrogenated (30 psi, 180°C, nickel–chromium catalyst) to yield normal butyl alcohol. For details of the aldol reaction, see *Crotonaldehyde.*

Some *n*-butyl alcohol is obtained in the high-pressure oxidation of propane and butane (see *Acetaldehyde* and *Formaldehyde*).

Secondary and tertiary butyl alcohols are produced by the absorption of butylene and isobutylene in sulfuric acid, similar to the production of isopropyl alcohol from propylene (see *Isopropyl Alcohol*).

Isobutyl alcohol is produced primarily as a by-product of the synthetic-methanol process (see *Methanol*). However, it is also a constituent of fusel oils, and some isobutyl alcohol is obtained in their separation (see *Amyl Alcohol* and *Ethyl Alcohol*). Recently, it has also been produced as one of the products of hydrocarbon oxidation (see *Acetaldehyde*).

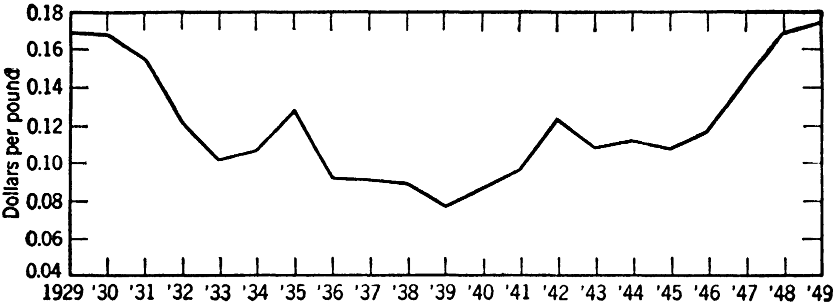


Production—Butyl Alcohol

Use Pattern

Normal and primary butyl alcohols	Per cent
Chemical manufacture (chiefly esters)	70
Lacquer solvent	15
Miscellaneous and export	15
	100

Secondary butyl alcohol	1947 (est.), per cent
Methyl ethyl ketone	90
Solvent and other	10
	100



Price—Butyl Alcohol, Normal

Miscellaneous

Properties. *n-Butyl alcohol* ($CH_3CH_2CH_2CH_2OH$). Colorless liquid possessing a vinous odor.

Mol. wt.	74.12	M.P.	−79.9°C
Sp. gr.	0.810 20°C/4	B.P.	117.7°C

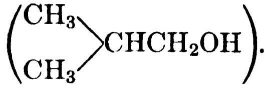
Weight per gallon 6.75 lb (20°C)

Soluble in alcohol and ether in all proportions at room temperature. Slightly soluble in water (9 g per 100 ml at 15°C).

Flash point (closed cup)	100°F
Ignition temperature	650°F
Vapor density (air = 1)	2.55
Explosive limits (% by volume in air)	Lower 1.7
	Upper —

Grades. Technical (98 to 100%).

Containers and Regulations. Tank cars, tank trucks, drum cars, compartment tanks, steel drums, cans, and bottles. No ICC shipping label required.



Properties. *Isobutyl alcohol* $\left(\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}\!>CHCH_2OH\right)$. Colorless, mobile liquid.

Mol. wt.	74.12	M.P.	−108°C
Sp. gr.	0.798 25°C/4	B.P.	107.9°C

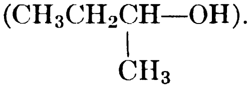
Weight per gallon 6.65 lb (25°C)

Soluble in alcohol and ether in all proportions at room temperature. Soluble in water (10 g per 100 ml at 15°C).

Flash point (closed cup)	82°F
Ignition temperature	800°F
Vapor density (air = 1)	2.55
Explosive limits (% by volume in air)	Lower 1.68 Upper —

Grades. Technical.

Containers and Regulations. Steel drums, barrels, and bottles. No ICC shipping label required.



Properties. *sec-Butyl alcohol* ($CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H{-}OH$). Colorless liquid with a strong, pleasant odor.

Mol. wt.	74.12	M.P.	−114.7°C
Sp. gr.	0.808 20°C/4	B.P.	99.5°C

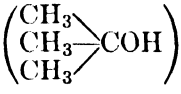
Weight per gallon 6.74 lb (20°C)

Soluble in water (12.5 g per 100 ml at 20°C), alcohol, and ether.

Flash point (closed cup) 75°F

Grades. Technical.

Containers and Regulations. Tank cars, drum cars, compartment tanks, steel drums, cans, and bottles. Red ICC shipping label required.



Properties. *tert-Butyl alcohol* $\left(\begin{smallmatrix}CH_3\\ CH_3\\ CH_3\end{smallmatrix}\!>COH\right)$. White crystals with a camphor-like odor.

Mol. wt.	74.12	M.P.	25.55°C
Sp. gr.	0.779 (26°C)	B.P.	82.9°C

Soluble in water, alcohol, and ether in all proportions at room temperature.

Flash point (closed cup)	52°F
Ignition temperature	892°F
Vapor density (air = 1)	2.55
Explosive limits (% by volume in air)	Lower 2.35 Upper 8.0

Grades. Technical (99 per cent).

Containers and Regulations. Steel drums, barrels, and bottles. Red ICC shipping label required.

Economic Aspects

Butanol, or *n*-butyl alcohol, was first produced on a large scale during World War I as a by-product of acetone production by the fermentation of cornstarch. Butanol was actually the by-product, even though two parts of butanol were produced for each part of acetone. Shortly afterward, the expanding lacquer industry created such a demand for butanol that acetone became the by-product. Today they must rightly be considered joint products.

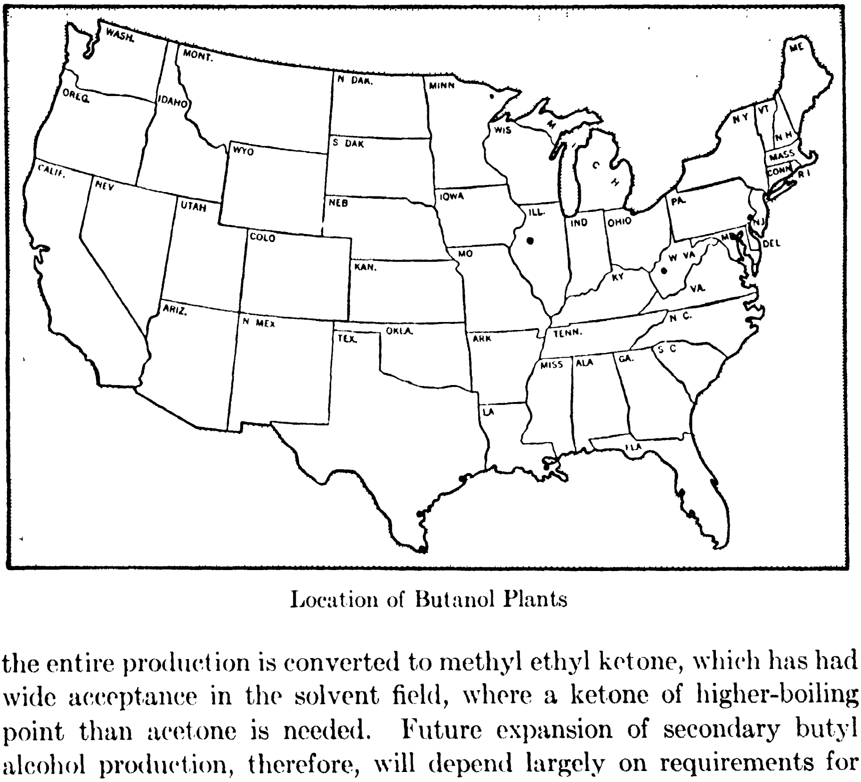
Competition between the fermentation and synthetic processes is becoming more acute with the latter showing gradual gains yearly. Production appears to be about equally divided between the two processes at present. The chief weakness of the fermentation process is the artificial price structure of the agricultural raw materials: corn and molasses. Hence, political considerations must be taken into account as a factor in raw-material price.

In the fermentation process, competition between corn and molasses as raw materials is also keen. It is probable that in normal times molasses has a slight edge. Regardless of whether corn or molasses is used, several by-products must be utilized for greatest economy. Both processes yield acetone, ethyl alcohol, stock feed, carbon dioxide, hydrogen, and riboflavin as by-products. The riboflavin is contained in the dried fermentation solubles (2 lb per lb mixed solvents) and sold for use in mixed feeds. Corn before mashing is degermed so that corn oil may also be a by-product. Considerable study has been made to utilize the evolved gases for ammonia, methanol, and acetic-acid production. An interesting recent patent has described a fermentation process using *Clostridium amylo-saccharo butyl propylicum* to produce a mixed solvent containing 70 per cent butanol, 3 per cent acetone, and 27 per cent isopropyl alcohol. Of course, different species and strains of the *Clostridium acetobutylicum* yield different ratios of butanol to acetone and ethyl alcohol.

The minimum economic size of a butanol fermentation plant is 10,000 gal of solvent per day, which is equivalent to about 15,000,000 lb butanol per yr. Plants usually have capacities of 20,000 to 30,000 gal total solvents per day. Synthetic plants may be built as small as 2,000,000 to 3,000,000 lb yearly capacity. Plants of this size may cost approximately $180,000 per 1,000,000 lb annual capacity.

The future of butanol production depends on price. The solvent field is becoming more highly competitive, but cheaper butanol will not only compete in this field but also be available for the synthetic organic-chemical industry. This industry itself will probably be the largest producer of butanol. On the other hand, the ease of conversion of a butanol fermentation plant to an ethyl alcohol distillery allows some flexibility.

sec-Butyl alcohol is made by essentially the same process as isopropyl alcohol, except that butylenes are used as the raw material. Practically the entire production is converted to methyl ethyl ketone, which has had wide acceptance in the solvent field, where a ketone of higher-boiling point than acetone is needed. Future expansion of secondary butyl alcohol production, therefore, will depend largely on requirements for methyl ethyl ketone (see *Methyl Ethyl Ketone*).



Location of Butanol Plants

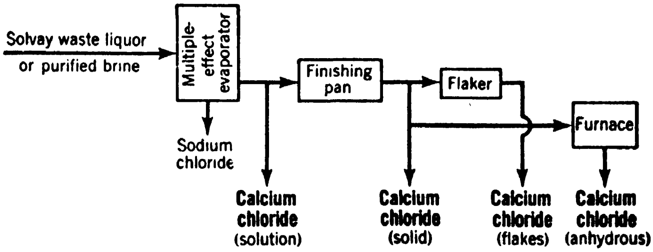
Isobutyl alcohol is one of the alcohols that occurs in fusel oil: 7.1 per cent of the total alcohols in fusel oil from molasses and 12 to 24 per cent of the total alcohols in fusel oil from corn. In late years fair quantities have been recovered as a by-product in synthetic-methanol plants. Chemical requirements for this alcohol have been fairly low, but during the war its use in hydraulic-brake fluid formulations increased tremendously. In this field, however, it must compete with a variety of newly developed special chemicals, and so the future is uncertain. Since the material is a by-product, price and therefore demand will be pegged to the price and availability of other alcohols in the same general boiling range.

Both isobutyl alcohol and butanol will be produced as by-products of the Fischer–Tropsch (Synthine) process. The impact of this additional production on present suppliers remains to be evaluated.

CALCIUM CHLORIDE

$CaCl_2$

From Solvay Waste Liquor or Natural Brine


Solvay waste liquor or purified brine
Multiple-effect evaporator
Sodium chloride
Finishing pan
Flaker
Furnace
Calcium chloride (solution)
Calcium chloride (solid)
Calcium chloride (flakes)
Calcium chloride (anhydrous)

Material Requirements

Basis—1 ton calcium chloride (75% solid)

Brine or liquor (9% $CaCl_2$)	17,000 lb

Process

Calcium chloride is obtained as a by-product in the ammonia–soda (Solvay) process and as a joint product from natural salt brines. The method of production is essentially the same in each process after the natural brines have been purified; that is, the calcium chloride-containing liquors are concentrated and crystallized.

Natural brines contain a mixture of calcium and magnesium chlorides, usually in a ratio of about 1 part magnesium chloride to 3 to 5 parts calcium chloride. For example, a typical analysis showing the principal constituents of a Michigan brine follows: approximately 14 per cent sodium chloride, 9 per cent calcium chloride, 3 per cent magnesium chloride, and 0.15 per cent bromine. The brine is generally treated to recover the bromine and sodium chloride. See *Bromine* for a more detailed description.

The brine that results from this treatment is rich in calcium and magnesium chlorides (*ca.* 3-to-1 ratio) and may be concentrated and crystallized to yield a calcium–magnesium chloride mixture. This product is suitable for some uses such as dust control. However, the presence of magnesium chloride tends to lower the melting point of the mixture, making it difficult to obtain a solid product. Magnesium chloride is also undesirable in refrigeration brine because it is corrosive.

The magnesium chloride is removed from natural brine by treating the liquor with calcium oxide (lime), which converts the chloride into the hydroxide. The magnesium hydroxide precipitates and is removed by settling and decantation or by use of countercurrent thickeners of the Dorr type. This process may be varied by removing the bulk of the magnesium chloride by fractional crystallization. The brine, containing a 1-to-3 weight ratio of magnesium and calcium chloride, is concentrated in evaporators to form the double salt: tachydrite. This salt, $2MgCl_2 \cdot CaCl_2 \cdot 12H_2O$, has a magnesium chloride–calcium chloride ratio of 2 to 1. The precipitation of the salt depletes the magnesium chloride content of the solution, until the equilibrium ratio of 1 to 10 (magnesium chloride–calcium chloride) is reached. The depleted mother liquor may be treated with lime (as previously) to remove the last traces of magnesium chloride.

Distiller waste liquor from the Solvay (ammonia–soda) process is practically free from magnesium chloride and requires no subsequent purification. The clear solution contains calcium chloride, sodium chloride, and a small amount of dissolved calcium sulfate. See *Sodium Carbonate* for details on the Solvay process.

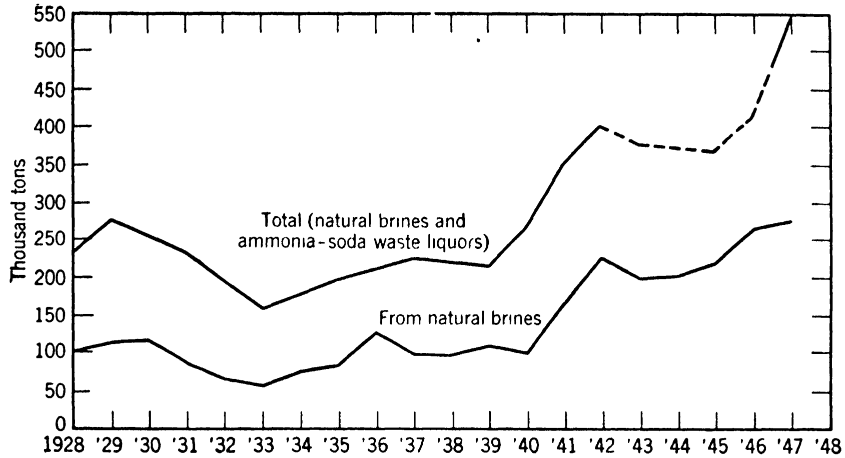
Natural brines, after purification, or the ammonia–soda waste liquors as they come from the plant are charged into triple-effect evaporators and concentrated. Both these raw materials contain sodium chloride, which is very slightly soluble in concentrated solutions of calcium chloride. Most of the salt, together with a small amount of calcium sulfate (Solvay liquors), crystallizes out in the first effect. After settling, the salt is discharged into centrifuges, washed, and packaged.

The evaporation is continued until the specific gravity of the liquor in the last effect reaches 42°Bé. Practically all the salt (sodium chloride) has crystallized at this point and can be settled out. The clarified liquor is decanted from the evaporator and pumped into a single-effect finishing pan or cast-iron pot, where it is concentrated further (until a solids content of about 75 per cent is reached). The molten mass is discharged into steel drums, where it solidifies on cooling. The product is known as 75 per cent calcium chloride and corresponds to the formula $CaCl_2 \cdot 2H_2O$. Alternately, the molten material may be run over a flaker, yielding 75 per cent calcium chloride flakes.

Anhydrous calcium chloride may be prepared by heating the 75 per cent calcium chloride in a reverberatory furnace or rotary calciner.

Some of the salt is decomposed, giving calcium oxide and hydrogen chloride. The evolution of the gas yields a porous mass of fused calcium chloride, which assays about 95 per cent. The cooled anhydrous material is crushed, screened, and classified before packaging.

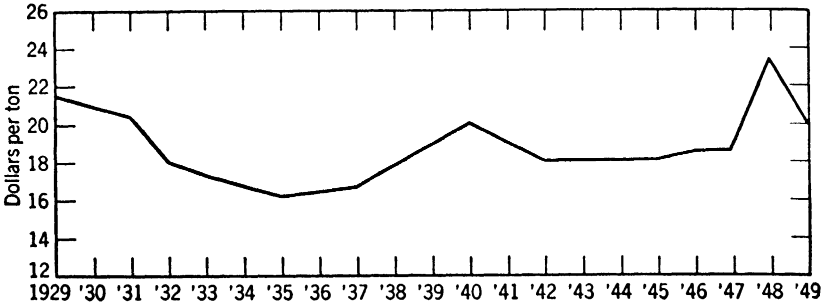
Calcium chloride solutions, used as cooling brines and antifreeze solutions, are withdrawn at various steps in the evaporation (concentration) process, depending on the specific gravity desired.



Production—Calcium Chloride (75%)

Use Pattern

	Per cent
Road treatment	60
Coal treatment	15
Concrete conditioning	5
Refrigerating brines	5
Miscellaneous	15
	100



Price—Calcium Chloride (75%)

Miscellaneous

Properties. White, deliquescent crystals, granules, lumps, or flakes.

Mol. wt.	110.99	M.P.	772°C
Sp. gr.	2.152 15°C/4	B.P.	>1,600°C

Soluble in water (59.5 g per 100 g at 0°C, 347 g per 100 g at 260°C), and alcohol. Forms various hydrates with water as follows:

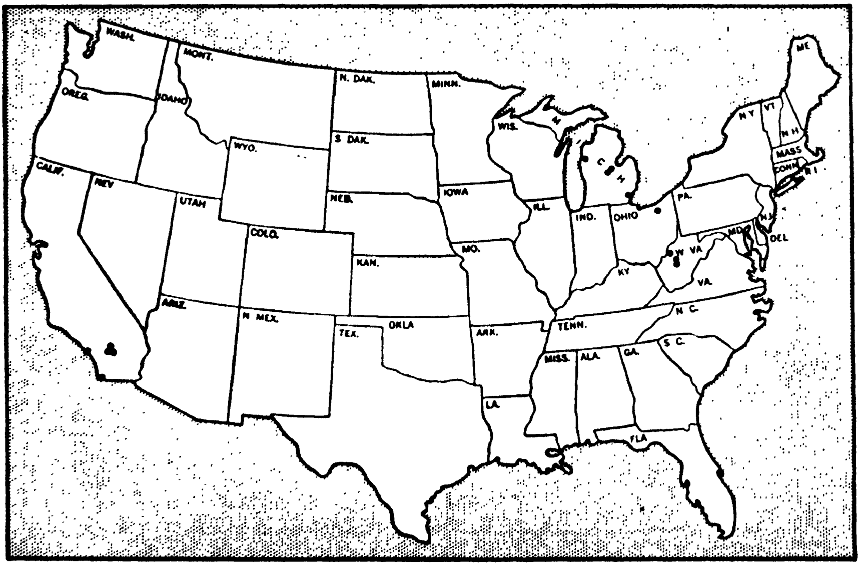
	Mol. wt.	Sp. gr.	M.P.	B.P.
Monohydrate ($CaCl_2 \cdot H_2O$)	129.01		260°C	
Dihydrate ($CaCl_2 \cdot 2H_2O$)	147.03			
Hexahydrate ($CaCl_2 \cdot 6H_2O$)	219.09	1.68 (17°C)	29.92°C	Loses $6H_2O$ at 200°C

Grades. C.P., USP, and technical in the form of solid (73 to 75 per cent), powder (77 to 80 per cent), flake or pellets (77 to 80 per cent), and liquid (38.6 per cent).

Containers and Regulations. Tank cars (liquid), drums, bags, and bottles. No ICC shipping label required.

Economic Aspects

Calcium chloride is a by-product of either the ammonia-soda process or of the processing of salt brines. In 1948 there were 11 producers of natural calcium chloride and only two ammonia-soda producers. All ammonia-soda plants, of course, could work up their calcium chloride



Location of Calcium Chloride Plants

brines if they so chose. The amounts recovered depend on market requirements, marketing facilities, and transportation costs. Few radically new uses are apparent at the present time, but increased road construction in the next few years may add to demand, not only as a stabilizer, but also as an antifreeze and early strength additive in cement. The use of calcium chloride solutions in tractor tires (to increase weight and improve traction) is expanding and may become a stable market. Considerable research work has also been done on the utilization of calcium chloride as a fog disperser in harbors and over airports. Whether or not such use is practical has not yet been proved.

Approximately equivalent amounts of calcium chloride are produced from each of the two sources, although that recovered from the ammonia–soda process has the advantage of being free of magnesium chloride. The magnesium-free product is usually specified for refrigeration brines because of the corrosive characteristics of the magnesium salt.

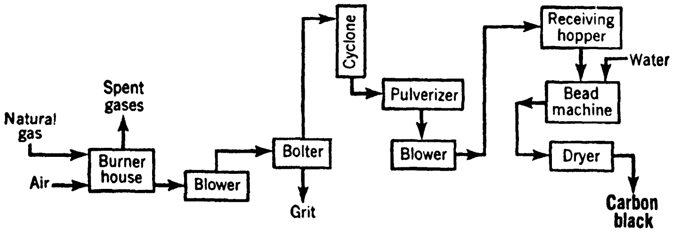
Although calcium chloride is always a by-product, its price remains fairly high because of the high cost of recovery.

CARBON BLACK

(COLLOIDAL CARBON)

C

From Natural Gas (Channel Process)



Reaction

$$CH_4 \rightarrow C\ (\text{amorph}) + 2H_2$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

3 to 5% yield; 1 to 1.5 lb per 1,000 cu ft

Basis—1,000 cu ft gas containing 31 lb C

Material Requirements

Basis—1 ton carbon black

Natural gas	1,600,000 cu ft

Process

Channel black, one of the three principal types of carbon black, is produced by the incomplete combustion of natural gas in small flames, which impinge on cooled channel irons.

Natural gas, as taken from wells, is usually passed through gasoline absorbers where either mineral or seal oil strips it of its gasoline content. The recovery of valuable gasoline aids in the economics of carbon-black plants and has no appreciable effect on the quality or quantity of black produced.

The "dried" gas, consisting chiefly of methane, is then piped (1¼-in. pipe) to burner houses—long, low sheet-iron buildings containing several thousand lava-tipped burners. The natural gas, at controlled pressures varying from 0.2 to 1.5 in. water, issues through a small slot (*ca.* 0.4 in. wide) in the ceramic tips (of about ⅜ in. outside diameter) and is burned in an insufficient supply of air. The amount of air is controlled by dampers at the bottom and top of the burner houses to give a luminous smoky flame, which impinges on the flat underside of moving cool channel irons. Here the temperature of combustion, 1,000 to 1,200°C, is reduced to about 500°C, and the carbon black is deposited. The channels (6 to 8 in. wide) are constructed of mild steel and move continuously backward and forward on overhead rails.

The deposited carbon black is removed as the channels pass over stationary scrapers. Falling into hoppers, it is carried by screw conveyers to a central packing house. The spent gases, containing considerable quantities of black, escape through the stacks into the air.

In a central packing house, which services many units (a typical plant would have 30 or more burner houses per unit and up to 10 or 12 units in one plant, utilizing a single blending and packing house), the soft, fluffy mass, which weighs only about 3 lb per cu ft, is "bolted." In this operation the grit, scale, and coarse particles are removed by screening through silk bolting cloth. The carbon black, after being blown through the bolting machines, is collected in an expansion tank and then carried by a screw conveyer to a pulverizer, where it is ground to a more uniform size. It is then blown into a receiving tank, from where it is conveyed into a bead machine. Here a dustless carbon black is made by adding a small amount of water (less than that needed to form a free meniscus) and running the resulting paste over a table containing small rotating pins. The colloidal black agglomerates under the constant agitation and forms small pellets or beads bulking at about 27 lb per cu ft. The beads are dried in a rotating cylinder (*ca.* 30 ft long) at approximately 150°F and transported by a bucket elevator to a combination storage and loading tank. The pelleted carbon black is then packaged in paper bags or in specially designed tank or hopper cars.

Less dense grades of channel black are made by agitating the light fluffy mass after it comes from the bolting machines. This operation produces a commercial grade known as uncompressed black, which has a density of about 13 lb per cu ft. Although suitable for some inks and paints, the uncompressed grade must be further compacted to reduce the tendency to dust if it is to be used in the rubber industry.

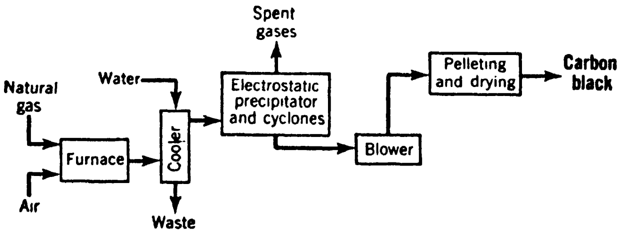
Both a semicompressed grade, bulking about 21 lb per cu ft, and a more widely used form, a double-compressed or heavy-compressed grade, which has a density of approximately 25 lb per cu ft, may be produced.

Other processes producing carbon black by impingement of flames are used to a minor degree. The disk process employs a small rotating disk (3 ft in diameter) as the depositing surface, whereas the Cabot process makes use of stationary plates (about 24 ft in diameter). Both are similar to the channel method; the differences involve the nature of the depositing surfaces and the scrapers.

A third method, the roller or rotating-cylinder process, produces a type of black utilized by the ink industry. Gas burners furnish cylindrical flames, which impinge on rotating rollers located directly overhead. The cast-iron rollers, 3 to 8 ft in length, 8 to 9 in. outside diameter; rotate slowly. Deposited carbon black is continuously removed by direct-contact scrapers, which run the entire length of the rollers and are located near the top. The black falls into trough-shaped collecting hoppers located beneath the rollers and is removed for processing by screw conveyers.

Various types of carbon black are made by changing the size of the burner tips, the gas pressure, the height and shape of the flame, the area and type of depositing surface, and the velocity of motion of the surface. These various types of black are offered in different grades, which depend on the amount and method of compacting, for example pelleting.

From Natural Gas (Furnace Process—Combustion)



Reaction

$$CH_4 \rightarrow C \text{ (amorph)} + 2H_2$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

30 to 40% yield; 9 to 12 lb per 1,000 cu ft

Material Requirements

Basis—1 ton carbon black

Natural gas	200,000 cu ft
Air	800,000–1,200,000 cu ft

Process

Furnace black, the second principal type of carbon black, is made by continuous processes involving partial combustion or a combination of combustion and thermal cracking of natural gas (in some cases mixed with oil) in furnaces of special design.

Natural gas, after passing through gasoline absorbers, is introduced into a horizontal or vertical furnace with a regulated amount of air. Here it is partially burned in multiple free flames, resulting in the formation of carbon black and gaseous products. The gaseous stream is passed through an air-cooled flume into a spray cooler, where the temperature is reduced by water. The carbon black is separated from the combustion gases by means of Cottrell precipitators and a battery of cyclone collectors. The gas vented to the air is substantially free of black.

The fluffy carbon black is transported by a screw conveyer to a blower or bucket elevator, which transports it to pelleting equipment. Here the black may be pelleted dry by rotating drums or wet by several processes. In one wet process the furnace black and water are mixed to form a pasty mass, which is then agitated in a trough by a series of pins on a rotating shaft (see *Channel Black*). In a second process the black is pelleted wet in a special trough mixer, from where it is given a final pelleting in a rotating cylinder.

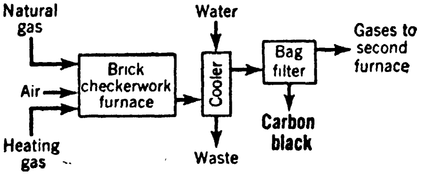
The beaded furnace black, although not so sturdy as some channel blacks, may be packaged in bags or bulk-packed in covered hopper cars.

Various yields and qualities of black are produced by controlling such factors as composition of raw material, furnace design, degree of turbulence, amount of secondary air, temperature, and contact time. The versatility of the process has resulted in about seven different methods of effecting partial combustion or combustion–thermal decomposition of gases in furnaces of various designs. Five important variations are described in the following. The first method consists of introducing relatively cold hydrocarbon gas by means of several jets into a furnace containing a turbulent flow of hot gas burning at or above 2,400°F, which decomposes the hydrocarbon gas to form finely divided carbon particles. The second method makes use of a horizontal furnace with air ducts spaced alternately with special burner ducts, through which hydrocarbon gas is introduced in relatively thin spaced columns. These parallel streams of air and gas move upward within an unobstructed, heated space where adjacent streams of air and gas make interfacial contact, with a minimum of turbulence, to develop a high temperature and to form a flame front around the gas streams. In this manner heat is supplied for decomposition of the hydrocarbon within the flame fronts to form the furnace black. A third method utilizes a mixture of air and natural gas in such proportions that partial combustion of the gas is accomplished in horizontal furnaces or converters having specially designed inlets. These allow adjustment in the volume, velocity, and direction of the gas and air, thus permitting partial combustion in a vigorous, swirling mass of flame, which moves through a reaction chamber at a controlled rate. The type and yield of black produced depend on the temperature (in the reactor), which is regulated by the extent of combustion permitted.

In the fourth variation of the process, a liquid hydrocarbon is partially vaporized in a combustion chamber and fully vaporized in a second chamber by direct heat exchange with the flame from the combustion chamber. The vapors are passed together with air into a reaction chamber, where the mixture is burned at a temperature sufficiently high to produce carbon black.

A fifth procedure uses a specially constructed retort, which operates at a high temperature. A stream of liquid hydrocarbon is forced under high pressure through a spray nozzle into the retort, where it is vaporized; part of the vapors are burned, and the remainder are cracked to give carbon black.

From Natural Gas (Furnace Process—Thermal Decomposition)



Reaction

$$CH_4 \rightarrow C\ (\text{amorph}) + 2H_2$$

30% yield; 10 lb per 1,000 cu ft

Material Requirements

Basis—1 ton carbon black

Natural gas	200,000 cu ft

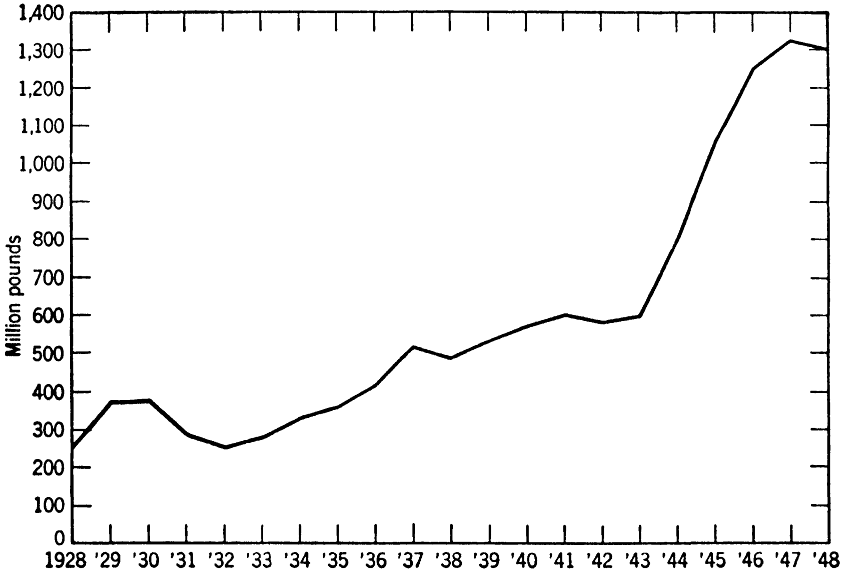
Process

Thermal blacks, the third principal type of carbon black, are made by thermally cracking natural gas by a cyclic process in a furnace previously heated by the combustion of a gas–air mixture.

Natural gas is introduced near the top of a furnace (about 14 ft outside diameter and 25 ft high), from where it passes downward over heated bricks (above 1,600°F) arranged in a checkerwork design. The gas is split into its elements, carbon and hydrogen, in a reducing atmosphere of essentially pure hydrogen. About half the carbon remains on the brickwork; the remainder is carried by the gaseous hydrogen stream through a water cooler into a bag filter, where the carbon black is collected in fabric bags. The black is then conveyed to storage hoppers.

After a short period the natural gas is turned off, and the hydrogen from the filters is reintroduced into the furnace (actually it goes to a second furnace) for the heating cycle. Natural gas and air are mixed with the hydrogen and passed through the checkerwork, igniting the carbon on the firebricks. After reaching temperature, the heating gas is shut off, and natural gas is again introduced, thus completing the cycle.

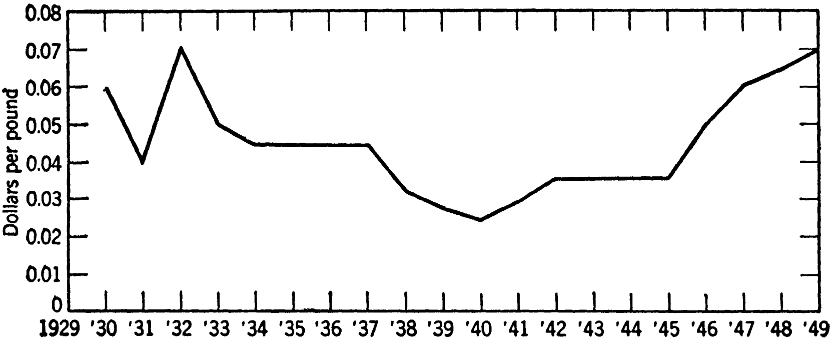
A modification of this process uses refinery waste gases to produce hydrogen for ammonia synthesis (see *Ammonia*) and obtains carbon black as a by-product. The furnace, a vertical converter filled with refractory material, is heated by means of natural gas supplied to burners with air being forced into the converter adjacent to the burners. After the heating cycle, the refinery gases are introduced for the make cycle.



Production—Carbon Black

Use Pattern

	1948 (est.), per cent
Rubber	67.5
Ink	2.6
Paints	0.5
Miscellaneous and export	29.4
	100



Price—Carbon Black (Beads, c. l.)

Miscellaneous

Properties. Fluffy, black, amorphous powder.

Mol. wt.	12.01	M.P.	>3,500°C
Sp. gr.	1.8–2.1	B.P.	4,200°C

Insoluble in cold water, hot water, acids, and alkalies.

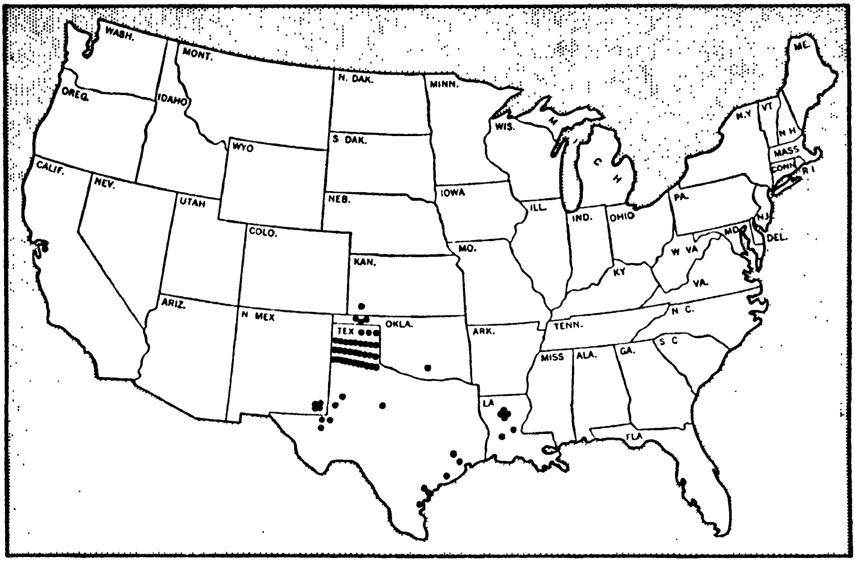
Grades. Various, depending on source, fineness, and color. Among the more important grades for rubber compounding are: channel, conducting (CC); channel, hard processing (HPC); channel, medium processing (MPC); channel, easy processing (EPC); furnace, conducting (CF); furnace, fine (FF); furnace, high modulus (HMF); furnace, high elongation (HEF); furnace, reinforcing (RF); furnace, semireinforcing (SRF); thermal, fine (FT); thermal, medium (MT); acetylene; lampblack.

Containers. Bags and hopper cars. Recently, in special polyethylene bags.

Economic Aspects

Before World War II, about 80 per cent of the carbon black manufactured was channel black, the rest being made up of furnace black (beginning in 1928) and the various special blacks. Because of the demand for furnace black by the synthetic-rubber industry, these figures changed in 1946 to about 51 per cent furnace black and 49 per cent channel black.

The relative future importance of the two blacks, as well as the importance of carbon black in general, is intimately related to the rubber industry. Synthetic rubber requires 950 lb carbon black per long ton, and natural rubber 400 lb. Channel black is apparently satisfactory for natural-rubber compounding, so that competition between blacks may be regulated by synthetic- versus natural-rubber competition. On the other hand, with increasing gas prices, new pipeline outlets for natural-gas fields, and the great yield advantage of furnace black (10 to 30 per cent) over channel black (3 to 5 per cent), prices of the two blacks may be brought closer together, to the competitive advantage of furnace black even in natural rubber. In 1943, carbon-black plants used 10 per cent of the natural gas consumed in the United States.



Location of Carbon-Black Plants

Plants are usually quite large in size, varying from 3,000 to 50,000 tons annually, with most plants between 5,000 and 10,000 tons annual capacity. Complete plants in the 10,000-ton range cost about $100 per annual ton capacity, with channel plants lower and furnace plants higher. Small channel plants of sixty 50-lb bbl daily capacity (500 tons per year), built in the early days of the industry, would cost about $500 per annual ton if built today.

Besides channel black and furnace black, a number of minor special blacks are made and marketed, such as roller black for certain inks, lampblack for carbon brushes, and acetylene black for explosives and dry cells.

Channel-black plants are notorious for the black sooty pall that hangs in the atmosphere above them and, consequently, must be situated in sparsely populated regions. If and when population shifts toward such plants, legal difficulties may be expected.

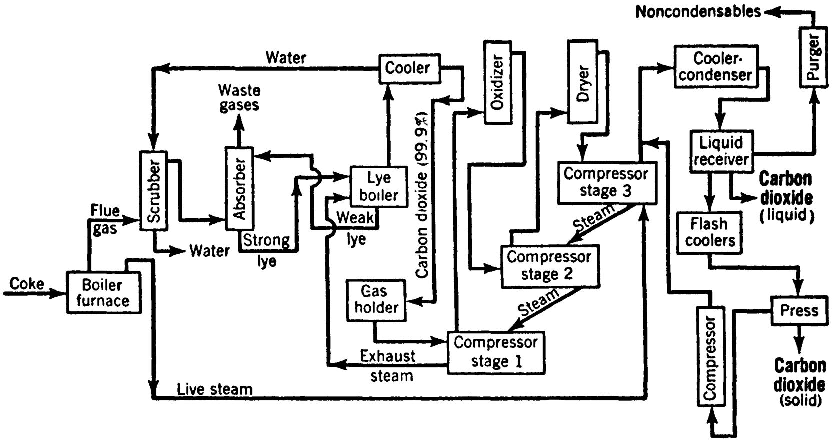
A possible future factor in carbon-black demand is the development of silica white, which is said to be equivalent in all ways to carbon black in rubber compounding but without, of course, its discoloring properties. At present, the cost differential is prohibitive, but the material is nevertheless a threat of considerable magnitude.

On the other hand, it is quite possible that the cheaper grades of carbon black may find a wide use for the protection of soil and plants in cold weather. This could be a large outlet.

CARBON DIOXIDE

CO_2

From Flue or Kiln Gases by Absorption



Reaction

Combustion: $C\ (\text{amorph}) + O_2\ (\text{air}) \rightarrow CO_2$

Thermal decomposition: $CaCO_3 + \text{Heat} \rightarrow CaO + CO_2$

Recovery: $CO_2 + Na_2CO_3 + H_2O \rightarrow 2NaHCO_3$

$2NaHCO_3 + \text{Heat} \rightarrow Na_2CO_3 + H_2O + CO_2$

100% yield by weight from coke

Material and Utility Requirements

Basis—1 ton solid carbon dioxide from 18 per cent flue gas

Coke *	2,000 lb	Steam	20,000 lb
Sodium carbonate	25 lb	Electricity	10 kw-hr
Water	20,000 gal		

* Soft coal (1 ton), fuel oil (180 gal) or natural gas (2,200 cu ft) may replace the coke.

Process

The primary sources of dilute carbon dioxide gas are gases from the decomposition of carbonates and the combustion of coke and other fuels. The resulting gases, ranging in carbon dioxide content from about 10 to 40 per cent, are treated by absorption to remove carbon dioxide. After the concentrated gas is purified, it is compressed and refrigerated to give liquid or solid carbon dioxide.

Because the thermal decomposition of limestone, dolomite, magnesite, marble, and similar materials yields gases containing 32 to 42 per cent carbon dioxide, by-product recovery is often carried out on kiln gases at cement and lime plants (see *Lime*). When limestone or dolomite is used as a raw material, however, about 250 lb of coke is ordinarily mixed with every ton of limestone burned to effect fuel economy.

Flue gases resulting from the combustion of carbonaceous materials such as coke, coal, oil, and natural gas serve as another major source of carbon dioxide. Usually these raw materials are burned carefully to produce a gas containing 17 to 18 per cent carbon dioxide, and the heat obtained is converted into power to run the compressors. Although the following describes the recovery of carbon dioxide produced by burning coke, it is applicable to all raw materials that yield a gas of purity below 99.7 per cent.

Coke is burned under specially designed boilers in a Carborundum-lined furnace. Combustion is controlled by drafts (about 10 cu ft air per lb coke), so that the flue gases contain 17 to 18 per cent carbon dioxide. At the same time steam (125 to 150 psi) is generated in the boilers to furnish power for the pumps and compressors and heat for the lye boiler (see the following).

The hot (450°F) flue gases, containing oxygen, carbon monoxide, nitrogen, dust, and some sulfur and organic compounds, in addition to 18 per cent carbon dioxide, are passed through a heat exchanger and economizer (neither unit is shown in the flowsheet). Here the temperature of the gases is reduced to about 250°F, and the excess heat is taken up by countercurrently flowing strong lye. The gases are scrubbed in limestone-packed towers with water from the coolers to remove sulfur dioxide and dust and to reduce the temperature to about 100°F. The dilute carbon dioxide gas is then fed into the bottom of coke-filled absorption towers where it passes countercurrent to an aqueous solution of sodium carbonate (16°Bé) called "weak lye." After absorbing the carbon dioxide, the solution of bicarbonate, known as "strong lye," is pumped through heat exchangers operating at 220 to 250°F where the solution is heated before entry into the lye boiler. The absorbers, operating at about 85°F, remove all but about 9 per cent of the carbon dioxide in flue gas, which is then released to the atmosphere.

In place of sodium carbonate, other absorbents such as aqueous potassium carbonate (20°Bé), monoethanolamine (10 to 20 per cent), and triethanolamine may be used in a similar manner (see *Hydrogen—From Hydrocarbons and Steam*).

The preheated solution of sodium bicarbonate is heated with exhaust steam (from the compressors) in the lye boiler. Here, at a temperature of about 245°F, the bicarbonate is decomposed into sodium carbonate ("weak lye"), which is returned through the heat exchanger to the absorbers for re-use. The liberated gas, consisting of 99.8 per cent carbon dioxide, escapes through the rectifying section of the lye boiler, where it warms the entering "strong lye" solution. The gas passes through a water cooler, where the temperature is further lowered, and the moisture in the saturated gas is condensed and returned to the weak lye. The cooled gas is collected in a gas holder.

Before or during liquefaction, the concentrated gas is purified by removal of organic impurities which would affect its taste and odor, and the gas is dried. Various methods or so-called cycles of liquefaction are employed such as the precooling, binary, ternary, bleeder, or flush-cooling cycles. These operate on the raw gas or on a combination of raw and revert gases (return or back-blow gas from the solid carbon dioxide press), using two- or three-stage compression and either ammonia refrigeration or carbon dioxide flash cooling or a combination of both.

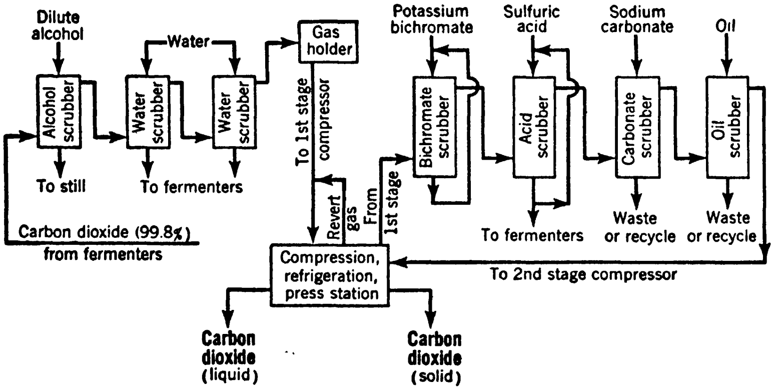
In the ternary cycle, the carbon dioxide from the gas holder is cooled to 40°F and raised to a pressure of 75 psi absolute in the first stage of the primary compressor. The compressors, usually two sets, are driven by live steam from the coke boiler, and the exhaust steam from them is used in the lye boiler.

From the first stage, the gas is passed through a purification system consisting of an oil separator and a scrubber, containing potassium permanganate or dichromate solution, which oxidizes organic impurities. The gas from the scrubbers, raised in temperature to about 50°F, enters the second compression stage and is discharged at a pressure of about 350 psi absolute. The temperature is lowered by water coolers to 40°F, at which point some of the water and vaporized lubricating oil (such as glycerine) are condensed. The gas passes through a desiccant drying tower (calcium chloride), where sufficient water is removed to prevent freezing of the valves. The gas is compressed to 970 psi absolute in the third stage, passed through a cooler, and liquefied in a condenser at 80°F (critical temperature is 88.43°F). Noncondensable gas is purged, and the 99.9 per cent liquid carbon dioxide, containing less than 0.1 per cent moisture and free from organic impurities, is either fed to flash coolers or charged into cylinders.

In two step-by-step flash coolers refrigerated by expanding carbon dioxide, the temperature is lowered first to 20°F and then to −40°F. The liquid carbon dioxide is fed to a metering tank and then to the solid carbon dioxide press. The liquid is allowed to expand through a nozzle forming "snow" in the chamber of the press. The vapors given off (revert gas) are utilized for precooling the liquid carbon dioxide going to the flash coolers. The gas is then recompressed in the secondary compressors and combined with the raw carbon dioxide at the same pressure.

The "snow" formed in the press is converted into a 220-lb, 20 × 20 × 10-in. block by lowering the upper ram under 2,500 psi until the block reaches the 10-in. thickness. Then the lower ram is dropped, and the block is ejected. After quartering by band saws, 55-lb 10-in. cubical blocks are wrapped in kraft paper and either stored or shipped in insulated cars.

From Alcohol Fermentation



Reaction

$$C_6H_{12}O_6 \xrightarrow{\text{Yeast}} 2C_2H_5OH + 2CO_2$$

Yield—1 bu corn or 6 gal molasses = $2\frac{1}{2}$ gal ethyl alcohol (190 proof) and 17 lb CO_2

Material and Utility Requirements

Basis—1 ton solid carbon dioxide

Carbon dioxide gas (99.8%)	Variable, depends on cycle	Oil	0.01 gal
		Water	2,000 gal
		Electricity	5.9 kw-hr
Potassium bichromate	0.5 lb	Steam (pumps only —compressors)	20,000 lb
Sodium carbonate	0.01 lb		
Sulfuric acid (66°Bé)	6 gal		

Process

Concentrated (99.5 to 99.9 per cent) carbon dioxide gas is obtained mostly as a by-product in the manufacture of ethyl alcohol by yeast fermentation of carbohydrates (see *Ethyl Alcohol*). Minor sources of the concentrated gas include escapage from natural springs and petroleum wells. The recovery of carbon dioxide differs from the foregoing system in that absorption is not required, owing to the high purity of the gas. No special cooling is necessary, because the temperature seldom exceeds 100 to 105°F.

The gas from sealed fermenters (or natural sources) is passed into the bottom of a stoneware-packed scrubber, where it passes countercurrent to dilute alcohol. Most of the entrained alcohol is removed from the gas and returned to alcohol stills for recovery. The gas then passes through two similar scrubbers, where the water-soluble impurities are removed by countercurrently flowing deaerated water. The water passes out of the bottoms of the scrubbers and is pumped to the fermenters for recovery of the alcohol. The partially purified gas is collected in a gas holder.

From the gas holder, the carbon dioxide is compressed to 75 psi absolute in the first stage of a three-stage compressor and passed through a series of scrubbers. In the first, the gas flows countercurrent to a potassium bichromate (or potassium permanganate) solution, which oxidizes the organic impurities such as aldehydes and higher alcohols. It is then scrubbed with concentrated sulfuric acid to complete the oxidation of the impurities and dehydrate the gas. The diluted sulfuric acid is pumped to the fermenters, where it is used to adjust the *p*H in the fermentation. Leaving the top of the scrubber, the gas contains some entrained acid, which is removed in a third scrubbing tower filled with coke. A solution of sodium carbonate flows downward in the tower, neutralizing the acid and releasing bound carbon dioxide. The gas then enters the bottom of the last scrubber, which contains a small quantity of an oil such as glycerine, which absorbs the oxidized impurities and delivers an odorless, tasteless gas. The purified carbon dioxide passes through the second stage of the compressor where its pressure is raised to about 400 psi absolute. The gas is cooled to about 0°F in a brine cooler and passes to the third stage, where it is raised to a pressure of 900 to 1,020 psi, depending on whether most of the gas goes subsequently to liquid or to solid form. After cooling in condensers to obtain liquid carbon dioxide, it is fed either to a cylinder filling stand or to flash condensers. In the latter the carbon dioxide is flashed off in successive steps until a temperature of −40°F and a pressure of 147 psi absolute is reached. The gaseous product evolved is condensed in ammonia-refrigerated coolers and combined with the cooled liquid carbon dioxide.

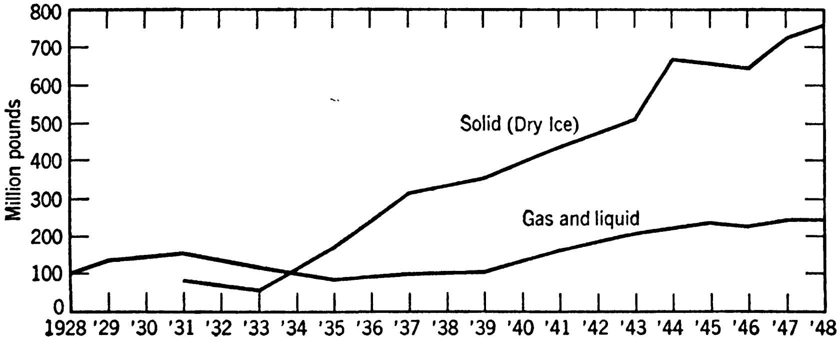
All the original gas from the compressor's third stage is liquefied and metered into a solid carbon dioxide press to form blocks. The revert gas from the press is returned to the system for recondensation.

Although the foregoing describes the Reich system of purifying and liquefying fermentation carbon dioxide, many variations may be introduced. The crude gas may be purified by adsorption of the impurities on activated carbon (Backhaus process) or on silica gel. Both these methods contain recovery systems for reactivating the adsorbent.

In addition, potassium permanganate may be used in place of the dichromate as the oxidizing medium, and a desiccant such as calcium chloride may be substituted for the sulfuric-acid dryer. Also, any one of a number of liquefaction systems may be employed. Instead of the Reich flash condensation cycle described, the process may use the ternary cycle outlined or any of several other cycles.

Carbon dioxide formed by the bacterial fermentation of carbohydrates to produce butyl alcohol and acetone (see *Acetone*) is also recovered by absorption. The gases produced contain about 60 per cent carbon dioxide and 40 per cent hydrogen. After the carbon dioxide is absorbed in one of the absorbing liquids (carbonates or alcohol amines), high-purity hydrogen is recovered (see *Hydrogen*).

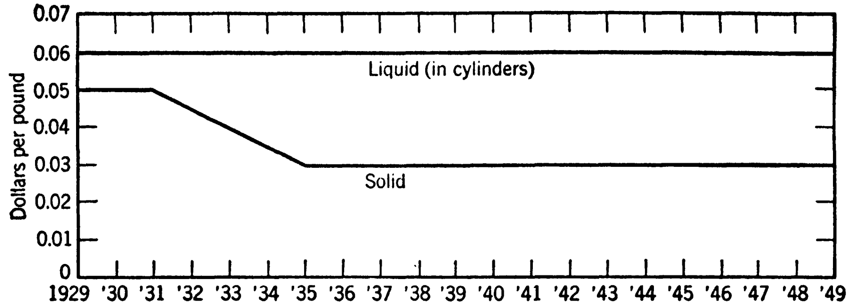
All the steps outlined may not be necessary for purifying the carbon dioxide gas obtained from natural springs. If the gas concentration is 99.7 per cent carbon dioxide or above, treatment may consist only of oxidizing and drying before compression. With dilute gases, however, the absorption system is used.



Production—Carbon Dioxide

Use Pattern

	Per cent
Ice cream and beverages	90
Miscellaneous	10
	100



Price—Carbon Dioxide

Miscellaneous

Properties. Colorless, odorless, noncombustible gas liquefiable to a heavy, volatile, colorless liquid, which may be compressed into a white snowlike solid.

Mol. wt.	44.01	M.P.	−56.6 (5.2 atm)°C
Sp. gr.		B.P.	Sublimes at −78.5°C
Gas	1.53 (air = 1)		
Liquid	1.101 (−37°C)		
Solid	1.56 (−79°C)		

Soluble in water (179.7 cc per 100 g at 0°C, 90.1 cc per 100 g at 20°C), acids, and alkalies.

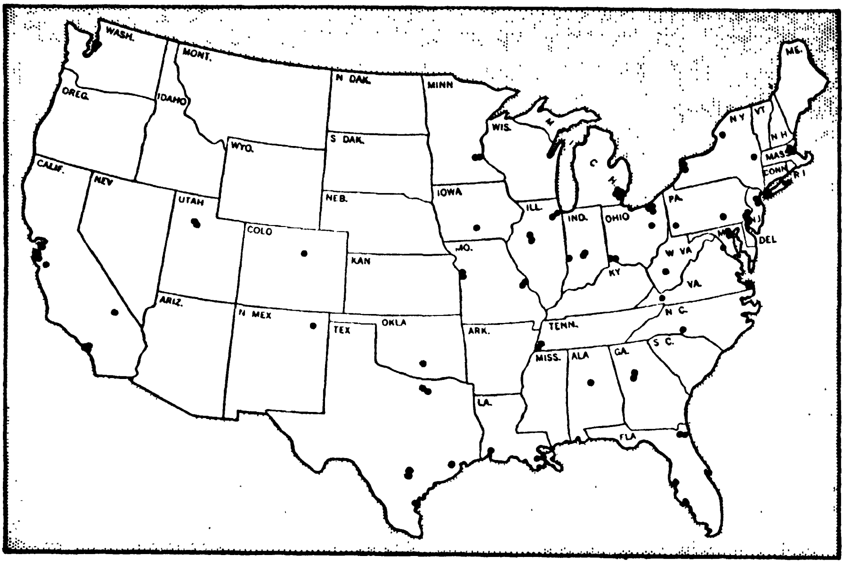
Grades. Technical in form of liquid (compressed gas); solid blocks (Dry Ice).

Containers and Regulations. Solid: bulk shipments (50-lb 10-in. cubical blocks) in special refrigerator cars and trucks. Liquid: steel cylinders. Green (gas) ICC shipping label required.

Economic Aspects

Carbon dioxide, both liquid and solid (Dry Ice), is one of those materials of such low bulk value and so widely used that it is manufactured in small or moderate-size plants in nearly every city in the United States. Despite the fact that the uses of both forms are legion, approximately 90 per cent of the total is used by the ice-cream and soft-drink industries. This demand is directly responsive to general economic conditions through the corner drugstore. It is interesting to note that, although solid carbon dioxide was unknown commercially in 1923, it now represents more than three fourths of the total carbon dioxide business in the United States. This percentage may be expected to increase in the future, since many users of liquid carbon dioxide have found it cheaper because of transportation costs to buy solid carbon dioxide and reliquefy it.

The process used for carbon dioxide generation depends on a number of factors, chiefly size and location of the plant. Small plants generally burn coke, although a few treat dolomite with acid, burn limestone, or recover carbon dioxide from natural springs. In the chemical industry, recovery of carbon dioxide from fermentation gases and lime burning are important (see *Ethyl Alcohol* and *Acetone*). Some carbon dioxide is recovered for resale in the ammonia–soda process (see *Soda Ash*). Natural gas may be used in place of coke as a raw material but yields lower carbon dioxide content in the burner gases (10 per cent versus 17 to 18 per cent for coke). The actual choice of a process depends on power and fuel costs at a given location.



Location of Carbon Dioxide Plants

Absorption of carbon dioxide from burner gases is usually done by soda-ash solutions, but recently the ethanolamines have entered the field, particularly in large installations. The chief drawback to the use of the amines is their corrosiveness toward iron and steel. Processes using silica gel and activated charcoal as gas adsorbent are also in use. Final dehydration of the gases may be obtained through use of calcium chloride, refrigeration, silica gel, or activated alumina.

The wide variation in raw materials and type of process is reflected in the range of plant costs. Moderate-size plants making both gaseous and solid carbon dioxide and making 500 lb carbon dioxide per hr (6 tons per day) may cost $2,000 to $15,000 per daily ton capacity.

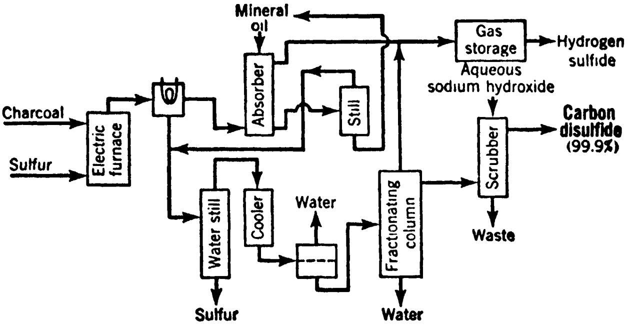
The outlook for increased production and use of all forms of carbon dioxide appears quite bright. In the small-plant field competition between local ownership and branch plants of larger companies may become quite keen. As a straw in the wind, one large manufacturer of industrial gases has recently built a large carbon dioxide plant near the plant of another large company manufacturing carbon dioxide fire-fighting equipment. Another new plant using monoethanolamine is recovering over 2,000,000 cu ft per day of carbon dioxide directly from a natural-gas supply which contains 16 per cent carbon dioxide. During the war, the isotopes plant at Oak Ridge used enormous quantities of solid carbon dioxide, and new fields are just beginning to open up in the frozen-food industry, in railway-car refrigeration, and in certain drying processes, such as in the manufacture of aspirin.

CARBON DISULFIDE

(CARBON BISULFIDE)

CS_2

From Sulfur and Charcoal



Reaction

$$C + 2S \rightarrow CS_2$$

35–40% thermal efficiency

Material and Utility Requirements

Basis—1 ton carbon disulfide

Charcoal (as theoretical carbon)	315 lb
Sulfur (theoretical)	1,685 lb
Electricity	800–1,000 kw-hr or equivalent fuel

Process

Carbon disulfide is produced by reacting charcoal and sulfur in the presence of heat furnished by electrothermal or retort methods.

In the electric-furnace process, dried charcoal is charged into the top of a vertical shaft located above the hearth in a specially constructed resistance-type furnace. Around this circular hearth are located four carbon electrodes, placed horizontally and symmetrically. The electrodes, each 4 ft long and 20 in. in diameter, are arranged so that they are about 1 ft apart in the middle of the furnace. Between the ends of the electrodes are pieces of charcoal or coke, which act as resistors. Sulfur is charged through channels in the walls of the hearth and in the shaft located near the furnace base. The furnace, which may vary in size from 240 to 330 kw at 60 volts and 4,000 to 6,000 amperes, is fed with two-phase alternating current, which generally passes between opposite electrodes. The thermal efficiency is 35 to 40 per cent.

At operating temperature (800 to 1,000°C) of the furnace, the sulfur vaporizes and reacts with the charcoal to form carbon disulfide and small amounts of by-products. The gaseous products pass up through the shaft to condensers, in which the carbon disulfide is liquefied. A high temperature is required to obtain a sufficiently fast reaction rate; it is controlled by regulating the voltage and rate of raw-material feed. To a certain extent, the furnace is automatically regulated by the sulfur, because, if the hearth becomes too hot, the sulfur in the channels rapidly melts, enters the hearth, rises above the electrodes, and, being a nonconductor, decreases the current.

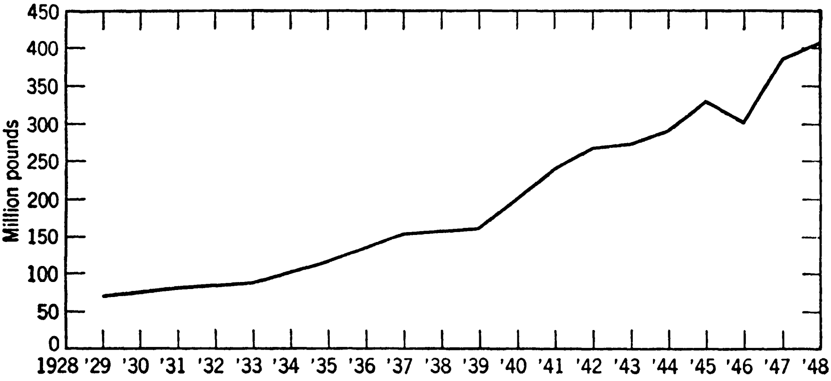
In the retort process, the reaction takes place in direct-fired retorts of cast iron or refractory firebrick. As in the electric-furnace process, previously dried charcoal is charged from the top, sulfur at the bottom, and, at a temperature of 800 to 1,000°C in the absence of air, carbon disulfide is formed. Usually natural gas or producer gas is used to fire the retorts, but any fuel may be employed.

The carbon disulfide gases formed in either type furnace pass through a side outlet in the shaft into coolers or water condensers. The uncondensed gases are fed into absorbers where countercurrently flowing mineral oil removes the residual carbon disulfide; the washed gases, mostly hydrogen sulfide, pass into storage tanks.

The absorbed carbon disulfide is freed from the mineral oil by distillation; the oil is returned to the absorbers for re-use, and the disulfide is combined with the liquefied carbon disulfide from the condensers. It is then run into continuous-distillation units. Here it may first be distilled in a hot-water still; the liquid crude disulfide is admitted by an aluminum spray nozzle. The disulfide volatilizes as it falls on the hot (80°C) water. Unreacted sulfur separates and falls to the bottom of the still. From here the gaseous carbon disulfide is cooled, the water is removed by decantation, and the cooled gas is passed into a fractionating column where residual hydrogen sulfide is removed. The hydrogen sulfide goes to the storage tank, from where it may be passed into a packed tower to be burned under reducing conditions, in the presence of a catalyst such as bauxite, to recover sulfur.

The fractionated carbon disulfide may be washed with 5 per cent caustic soda in a packed (porcelain rings) tower and condensed to give a 99.99 per cent product.

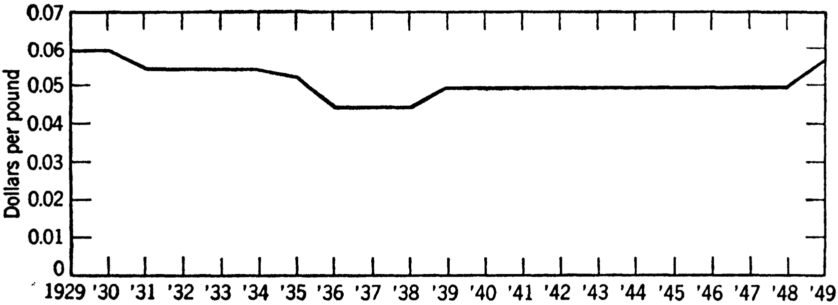
Another process has been developed in which natural gas is used as the source of carbon. With a catalyst such as activated alumina, containing a small amount of chromium oxide, carbon disulfide in yields of 90 per cent (based on methane charged) may be produced by reacting 1 mole of methane (natural gas) with 2 moles of sulfur at a temperature of approximately 700°C.



Production—Carbon Disulfide

Use Pattern

	1947 (est.), per cent
Rayon (viscose)	66
Carbon tetrachloride	16
Miscellaneous and export	18
	100



Price—Carbon Disulfide

Miscellaneous

Properties. Colorless, almost odorless flammable liquid. Commercial grade has a strong disagreeable odor.

Mol. wt.	76.13	M.P.	−108.6°C
Sp. gr.	1.263 20°C/4	B.P.	46.3°C

Weight per gallon	10.48 lb (25°C)

Soluble in alcohol, benzene, and ether. Very slightly soluble in water (0.2 per cent at 0°C, 0.014 per cent at 50°C).

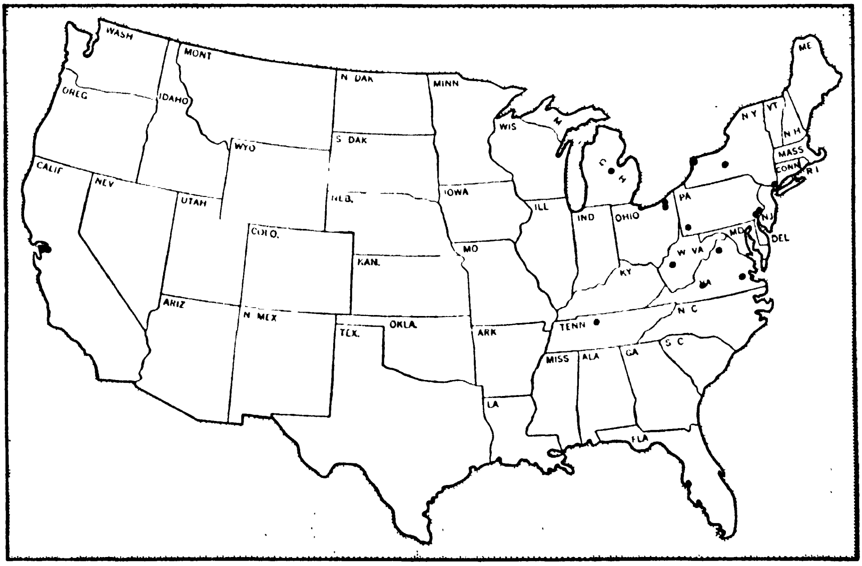
Flash point (closed cup)	−22°F
Ignition temperature	212°F
Vapor density (air = 1)	2.64
Explosive limits (% by volume in air)	Lower 1.0 Upper 50

Grades. Technical (99 per cent), and USP.

Containers and Regulations. Tank cars, drums, cans, and bottles. Red ICC shipping label required.

Economic Aspects

Carbon disulfide is largely a product of the electrochemical industry, since in most modern plants it is made in the electric furnace. Blast-furnace processes have been tried from time to time, and many are still in operation, but they are of doubtful economy.



Location of Carbon Disulfide Plants

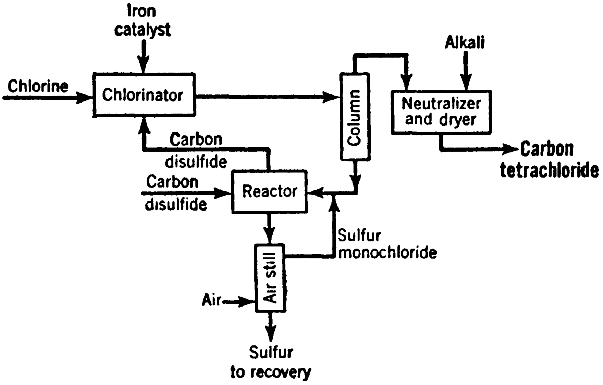
The greatest use of carbon disulfide is as a raw material in the manufacture of viscose rayon, which industry accordingly controls the demand for the chemical.

The smallest plant for economical production would be one based on a single furnace of 2,500 tons per year capacity. Most actual plants have capacities estimated at 10,000 to 15,000 annual tons. Plants of this size cost from $55 to $75 per annual ton capacity.

CARBON TETRACHLORIDE

CCl_4

From Carbon Disulfide and Chlorine



Reaction

$$CS_2 + 3Cl_2 \xrightarrow[\text{Catalyst}]{\text{Fe}} S_2Cl_2 + CCl_4$$

$$CS_2 + 2S_2Cl_2 \longrightarrow 6S + CCl_4$$

$$6S + 3C \longrightarrow 3CS_2$$

90% yield

Material Requirements (Major)

Basis—1 ton carbon tetrachloride

Carbon disulfide	1,100 lb
Chlorine	2,300 lb

Process

A solution of carbon disulfide in carbon tetrachloride (approximately 40 per cent carbon disulfide, 50 per cent carbon tetrachloride, and 10 per cent sulfur monochloride) is charged into a lead-lined chlorinator fitted with cooling coils. Chlorine is bubbled through the solution, which contains iron borings or powder as catalyst. The iron remains in the chlorinator from batch to batch and is replenished when warranted.

The temperature is maintained around 30°C by cooling water. An excess of chlorine is used to insure complete conversion of carbon disulfide (about 0.5 per cent remains unchanged).

The reaction products, consisting of carbon tetrachloride (60 per cent) and sulfur monochloride (40 per cent), are passed to a distilling column where they are separated. The carbon tetrachloride distillate, containing less than 1 per cent sulfur monochloride, is sent to a neutralizer and dryer where acidic materials are neutralized by agitation with alcoholic sodium hydroxide solution or by passage over alkaline desiccants. The moisture content is also decreased. Desiccants that may be used include anhydrous calcium chloride, sodium carbonate, and silica gel. The dried material may be redistilled if warranted to give carbon tetrachloride of 99.8 to 99.9 per cent purity.

The residue from the distillation column contains about 85 per cent sulfur monochloride and 15 per cent carbon tetrachloride. This mixture is reacted with carbon disulfide at 60°C in a lead-lined reaction kettle fitted with an agitator. At the end of the reaction, the carbon tetrachloride and most of the sulfur monochloride produced are distilled off. The distillate containing the afore-mentioned two compounds and unreacted carbon disulfide (about 40 per cent) is charged to the chlorinator to start the cycle.

The residual sulfur, containing 10 to 15 per cent sulfur monochloride, is discharged to an air still. The monochloride is removed by blowing with air and is recycled to the reactor. The recovered sulfur may be converted to carbon disulfide by reaction with coke (see *Carbon Disulfide* for details).

Several modifications of this process are existent. One such modification is the indirect chlorination of carbon disulfide with sulfur dichloride to produce carbon tetrachloride and sulfur. Less sulfur is produced by this method than by the direct chlorination since the following is the main reaction:

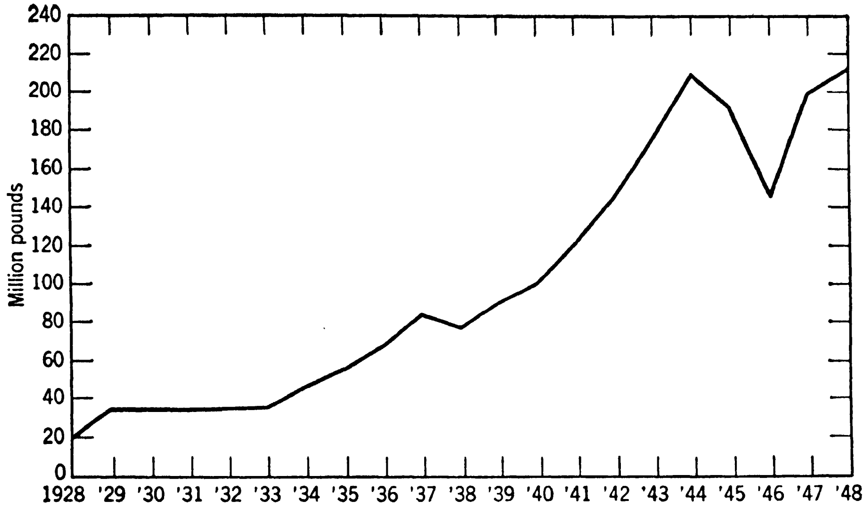
$$CS_2 + 2SCl_2 \rightarrow CCl_4 + 4S$$

The latter is chlorinated ($4S + 2Cl_2 \rightarrow 2SCl_2$) to yield sulfur dichloride, which is reacted with fresh carbon disulfide to complete the cycle. The carbon tetrachloride is removed from the sulfur by distillation and is purified as previously. The yield of carbon tetrachloride is approximately 90 per cent based on the weight of carbon disulfide.

From Hydrocarbons by Chlorination

Carbon tetrachloride is produced by the chlorination of methane and higher aliphatic hydrocarbons. If methane alone is used, small quantities of methyl chloride, methylene chloride, and chloroform are also obtained. Methane and chlorine gases are mixed and reacted at a temperature of 250 to 400°C. This may be accomplished by blowing the mixture of gases through an inert salt bath, which can be maintained at the desired temperature by cooling. Alternately, preheated chlorine gas may be added through a series of jets to a high-velocity stream of methane.

The velocity must be sufficient to exceed the rate of flame propagation so that the likelihood of explosion is reduced to a minimum. The main reaction ($CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$) is strongly exothermic, and cooling must be employed to prevent excessive temperature rise. At high temperatures, decomposition takes place with the deposition of carbon according to the following equation:



Production—Carbon Tetrachloride

$$CH_4 + 2Cl_2 \rightarrow C + 4HCl$$

This process requires corrosion-resistant metals and exacting controls. Nickel tubing has been found to be fairly satisfactory for the chlorination.

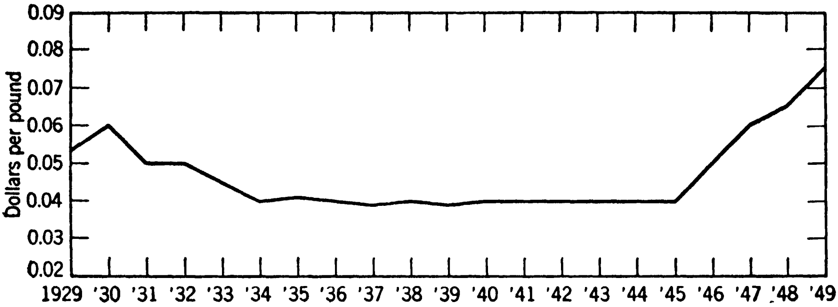
The reaction products consist of various chlorinated methanes, which must be separated by some appropriate method such as fractional distillation.

In one commercial operation, an initial gas-phase chlorination is run photochemically under such conditions that the main product is methyl chloride, although some methylene dichloride is formed. The product of this chlorination is condensed and subsequently photochemically chlorinated in the liquid phase in a cooled vessel. By proper selection of operating variables, the reaction can be made to yield predominantly either chloroform or carbon tetrachloride.

Carbon tetrachloride is also obtained as a by-product in the chlorination or chlorinolysis of higher hydrocarbons.

Use Pattern

	1947 (est.), per cent
Chemical manufacture (chiefly Freon)	35
Fire extinguishers	20
Dry cleaning	20
Agriculture (grain fumigation)	3
Miscellaneous and solvent	22
	100



Price—Carbon Tetrachloride

Miscellaneous

Properties. Colorless, nonflammable liquid with a peculiar odor.

Mol. wt.	153.84	M.P.	−22.6°C
Sp. gr.	1.595 20°C/4	B.P.	76.8°C

Weight per gallon	13.22 lb (25°C)
Vapor density (air = 1)	5.32

Soluble in alcohol, ether, chloroform, benzene, and petroleum ether. Very slightly soluble in water (0.097 per cent at 0°C, 0.08 per cent at 20°C).

Grades. Technical (99.5 to 99.9 per cent), USP, and C.P.

Containers and Regulations. Tank cars, drums, tins, cans, and bottles. No ICC shipping label required.

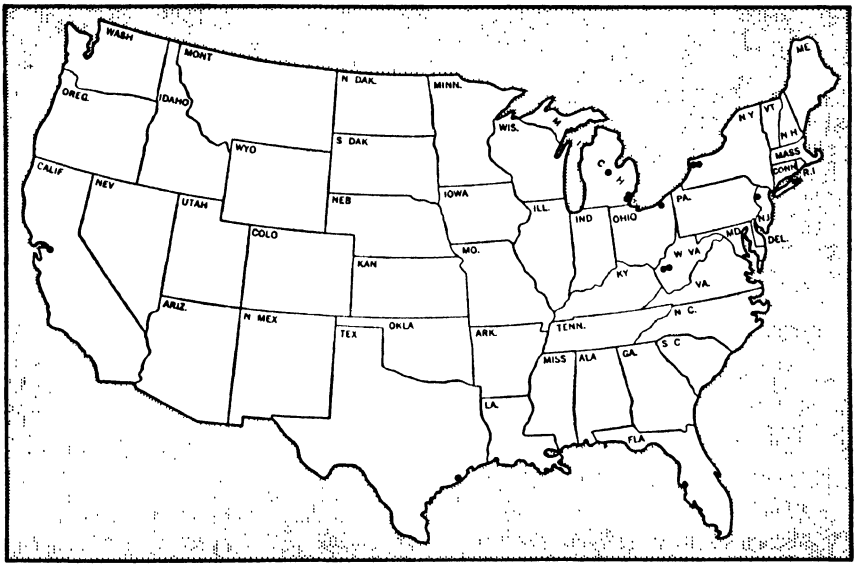
Economic Aspects

Carbon tetrachloride is one of several chlorinated hydrocarbons that may be used as a solvent for grease. In recent years, however, its use as a degreasing agent has declined because of competition with various chlorine derivatives of ethylene and acetylene. The effect of this competition may be felt even more in the future. Because of its inertness to oxidation, it is used to a considerable extent as a fire-extinguishing agent. The chief factor responsible for retaining the production level, however, is the need of carbon tetrachloride as a raw material for the refrigerant and insecticide dispersant: "Freon" (CCl_2F_2).

Of the two major manufacturing processes described, the carbon disulfide process is by far the most widely used, probably because it is much more easily controlled than methane chlorination and does not present so serious a by-product problem. It appears likely that the hydrocarbon chlorination process will eventually supplant the other because of inherent economies. In either case a cheap source of chlorine is imperative. Of the two process modifications employing carbon disulfide as a raw material, the process using sulfur monochloride is more widely prevalent than the one using sulfur dichloride. The former process is operated both on batch and continuous scales.

Some work has been done on a pilot-plant scale on the chlorinolysis of higher hydrocarbons to yield carbon tetrachloride as one of the products, but no commercial installations are known.

Actual plants vary in size from 2,000,000 to 50,000,000 lb per yr, with the most economic about 20,000,000 lb annually. Hydrocarbon-chlorination plants of this size cost approximately $30,000 per 1,000,000 lb annual capacity.

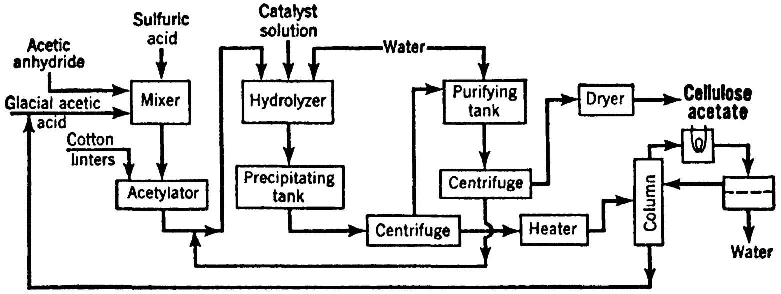


Location of Carbon Tetrachloride Plants

CELLULOSE ACETATE

$[C_6H_7O_2\cdot(OOCCH_3)_3]_x$

From Cellulose by Acetylation



Reaction

$$\underset{\text{Cellulose}}{[C_6H_7O_2\cdot(OH)_3]_x} + 3x(CH_3CO)_2O \rightarrow$$

$$\underset{\text{Cellulose acetate}}{[C_6H_7O_2\cdot(O_2CCH_3)_3]_x} + 3xCH_3COOH$$

85% yield

Material Requirements

Basis—1 ton cellulose acetate

Chemical cotton	1,400 lb	Acetic acid *	6,500 lb
Acetic anhydride	4,000 lb	Sulfuric acid	200 lb

Process

The action of acetic anhydride on chemical cotton produces cellulose triacetate. Various commercial grades of cellulose acetate, ranging from about 51 to 62.5 per cent acetyl content, are obtained by subsequent hydrolysis.

Chemical cotton, one of the raw materials, is about 98 per cent α-cellulose and is obtained by the purification and conversion of cotton

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* 10,000 lb recovered per ton cellulose acetate.

linters. The linters are short fibers, which are removed from the cotton seeds after the ginning operation. Cotton linters generally assay 80 to 85 per cent cellulose.

Bales of chemical cotton are pulled apart mechanically and may be either treated with acetic acid or dried, before charging into an acetylator. Approximately one part of chemical cotton is slowly added to 6 parts of an acetylating mixture maintained at 7 to 10°C. The mixture is prepared by adding equal parts of acetic anhydride and glacial acetic acid, plus a small amount of sulfuric acid as a catalyst, to a mixing tank. After cooling, the liquid is charged into the jacketed, glass-lined agitated cast-iron acetylator.

The acetylation temperature is kept below 30°C, and, after 5 to 8 hr, the viscous liquid is discharged into a hydrolyzer. Here the cellulose triacetate is allowed to hydrolyze to the desired degree by diluting with a little water containing acetic acid and sulfuric acid. The hydrolysis or aging is generally carried out at about 40°C and may take as long as 15 hr.

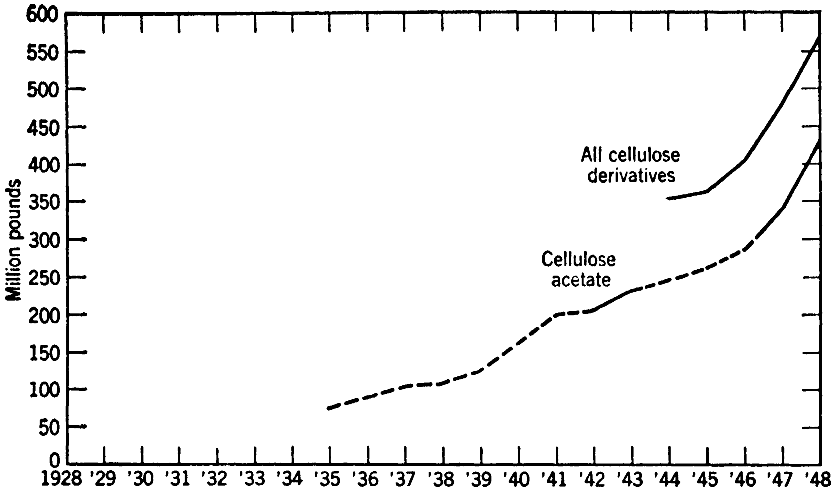
The hydrolysis is stopped by running the mixture into a large volume of water in the precipitation tank. The acetate is centrifuged from the acetic acid, which is recovered and re-used. After being washed several times with water, the cellulose acetate flakes are centrifuged and dried. The flakes may then be converted into molding powders, films, sheets, rods, tubes, solutions, or filaments for textiles.

Acetylation Using Internal Cooling

The method of acetylating cellulose described previously is limited in batch size by the cooling surface in the acetylator. In the last few years, an internal-cooling method has been adopted in some plants, in which methylene chloride is added with the acetylating mixture. Heat of reaction is carried away by vaporized methylene chloride, and much larger batches may be used. Lower concentrations of acetic anhydride may be used, and the reaction temperature may be raised, thereby reducing reaction time (4 to 6 hr at 50°C). A typical batch composition is:

	Lb
Cellulose	7,500
Acetic anhydride	22,500
Acetic acid	5,250
Methylene chloride	9,750
Sulfuric acid	75

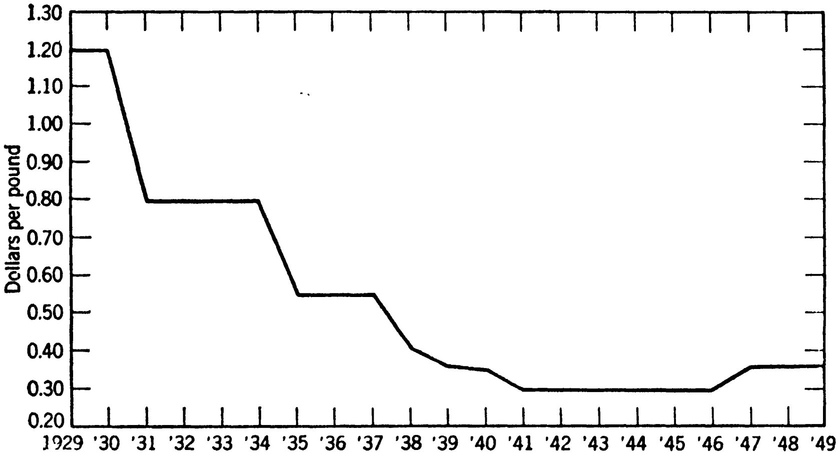
In the process, vaporized methylene chloride is continuously condensed and returned to the acetylator during the reaction. In the hydrolysis step all methylene chloride is distilled from the mass and recovered.



Production—Cellulose Acetate

Use Pattern

	Per cent
Fibers	75
Other plastics	25
	100



Price—Cellulose Acetate

Miscellaneous

Properties. White granular flakes or particles.

Per cent acetyl:	51	53	55	56	59	62
Approximate number of OH substitutions:	2.2	2.3	2.4	2.5	2.7	2.9
Sp. gr. 25°C/4	1.365	1.357	1.355	1.361	1.332	1.329
M.P. (penetration) °C		194	188	200	202	226

Soluble in acetone, methyl ethyl ketone, glacial acetic acid, chloroform, and various mixtures of organic solvents, depending on the degree of acetylation. Insoluble in water and alcohol. Resistant to weak acids, oils, greases, and fats. Not resistant to alkalies except at higher acetylations. Lower acetylations are resistant to chlorinated solvents.

Grades. Plastic, 52 to 54 per cent combined acetic-acid content; lacquer, 54 to 56 per cent combined acetic-acid content; film, 55.5 to 56.6 per cent combined acetic-acid content; water-resisting, 56.5 to 59.0 per cent combined acetic-acid content; triacetate, 60.6 to 62.5 per cent combined acetic-acid content.

Containers and Regulations. Bags and cartons. No ICC shipping label required.

Economic Aspects

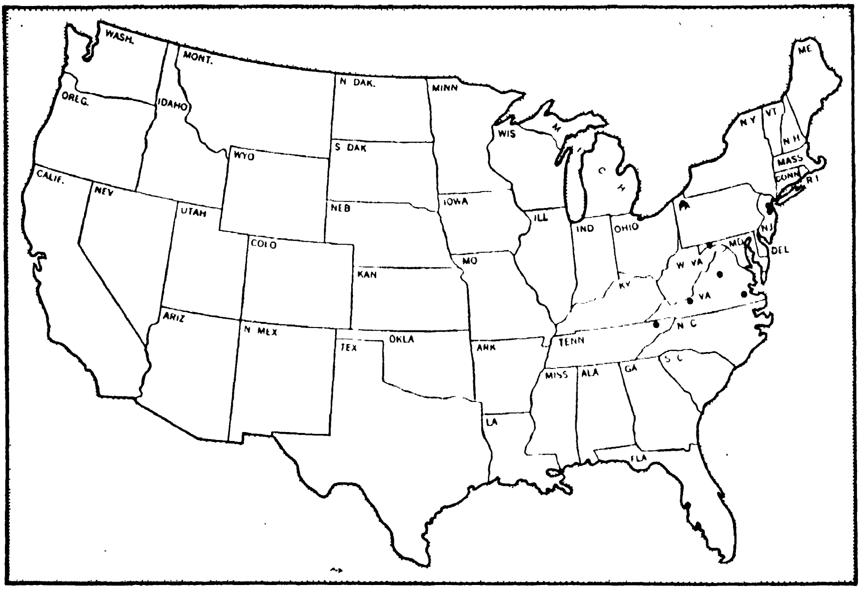
The early commercial use of cellulose acetate in the plastics, lacquer, and rayon industries was based on its slow-burning characteristics, compared with cellulose nitrate. Since its introduction, production has increased rapidly, and today it competes on a much wider basis. Its properties may be varied by the degree of acetylation, and products of varying specification are manufactured and sold. In the plastics field, it is the largest single material used for injection molding. It is also suitable for compression molding and continuous extrusion.

Transparency, lack of color, and resistance to heat and light are outstanding characteristics of cellulose acetate, in both plastics and lacquers. A disadvantage is poor general solubility in organic solvents.

Weather resistance is increased markedly by use of modified cellulose acetate such as cellulose acetate–butyrate. In the plastics field, similar derivatives, such as cellulose propionate and cellulose acetate–propionate, are gaining in popularity and will undoubtedly become cheaper as more propionic acid is available as a by-product of Fischer–Tropsch plants (see *Ethyl Alcohol*).

Large rayon and film manufacturers and some plastics manufacturers often make cellulose acetate for their own use. Smaller users purchase it in the form of flake or compounded with plasticizers for use in the making of plastics and lacquers. Economy demands that cellulose acetate be made on a large scale since recovery of acetic acid is an important cost factor.

In the fiber field, competition is keen with so many new fibers (nylon, Vinyon, protein fibers, and even glass fibers) entering the field. It is expected, however, that these newcomers will only widen the field of synthetic fibers and thus compete more with natural fibers (cotton, wool, silk, flax) than with other synthetic fibers. As far as existing synthetic fibers are concerned, cellulose acetate appears to have as firm a hold on the market as any other and as great possibilities for the future.



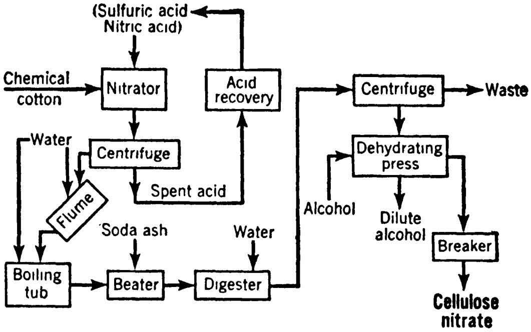
Location of Cellulose Acetate Plants

CELLULOSE NITRATE

(NITROCELLULOSE)

$[C_6H_7O_2(ONO_2)_3]_x$

From Cellulose and Nitric Acid



Reaction

$$\underset{\text{Cellulose}}{[C_6H_7O_2(OH)_3]_x} + 3xHNO_3 \xrightarrow{H_2SO_4} \underset{\text{Cellulose nitrate}}{[C_6H_7O_2(ONO_2)_3]_x} + 3xH_2O$$

80–85% yield

Material Requirements

Basis—1 ton cellulose nitrate (12.2% nitrogen)

Chemical cotton	1,500 lb	Sulfuric acid (100%)	1,000 lb
Nitric acid (100%)	2,000 lb	Sodium carbonate	5 lb

Process

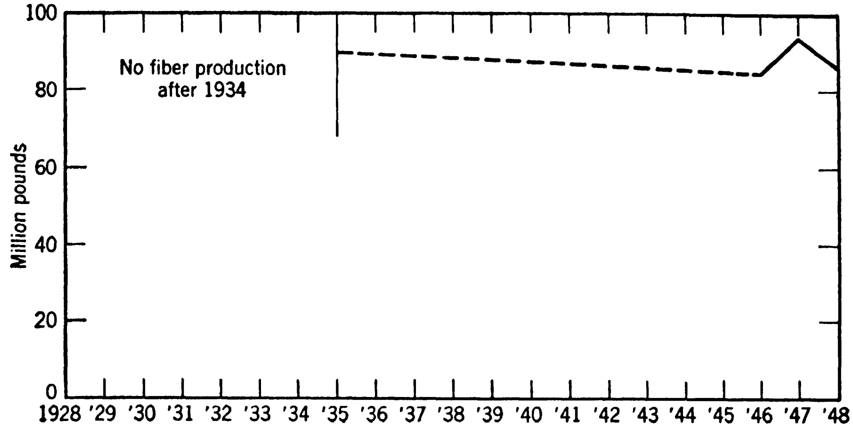
Cellulose nitrate, also known as nitrocellulose and pyroxylin, is produced by the action of nitric acid on chemical cotton in the presence of a dehydrating agent such as sulfuric acid.

Chemical cotton, a very pure form of α-cellulose, is produced from cotton linters, waste cotton, or specially purified sulfite pulp by bleaching, washing, and drying operations. The cotton is weighed and charged into a nitrator. Approximately 47 lb of mixed acid per lb of cellulose is then added. The mixture is agitated, the temperature being kept at about 30°C for 0.5 hr. The composition of mixed acid averages about 21 per cent nitric acid, 63 per cent sulfuric acid, and 16 per cent water.

At the end of the nitration period, which varies with the type of product desired, the charge is dropped into a basket centrifuge. The spent acid that is removed is fortified and re-used in subsequent batches. The nitrated cellulose is discharged as soon as possible into an immersion bowl and flume where it is drowned in cold water. The water carries the cellulose nitrate to a large tub. Here, the weak acid is drained off, fresh water is added, and the slurry is pumped to a "boiling tub." The material is boiled with at least four changes of water for as long as 40 hr. This series of boiling and washing treatments with purified water of controlled *p*H removes the retained free acid and destroys the unstable sulfate esters. The purified nitrocellulose is pulped by a beater and charged, with a dilute sodium carbonate solution, into a digester. The digesting or poaching operation is carried out in a long coil of alloy pipe, where the water-suspended cellulose nitrate is heated at high pressure for varying periods of time. This treatment reduces the viscosity probably by decreasing the chain length of β-glucose anhydride units in the nitrocellulose fibers. After additional washes to remove the decomposition products formed during the digestion, the purified product is centrifuged or allowed to drain in bins to remove most of the water. The product may be placed under pressure of 2,000 to 3,000 psi to remove more water. Final dehydration takes place by pumping ethyl alcohol through the cellulose nitrate held under pressure. The compressed blocks from the dehydration presses, wet with alcohol, are disintegrated by passage through a block breaker. The product is placed in shipping containers. Cellulose nitrate, containing about 12.2 per cent nitrogen, is then packaged by adding additional alcohol to the containers. Depending on the type of product obtained, the material is "colloidized" by adding alcohol, ether, diphenylamine, and other modifying agents during the packaging operations.

For nonexplosive uses, the cellulose nitrate, known as soluble nitrocellulose, is produced with a nitrogen content ranging from 10.7 to 12.2 per cent. This range is obtained by varying the ratio of the cellulose and mixed-acid raw materials and varying the concentrations of the individual acids. Different types according to viscosity are produced and result from changing the digestion operation.

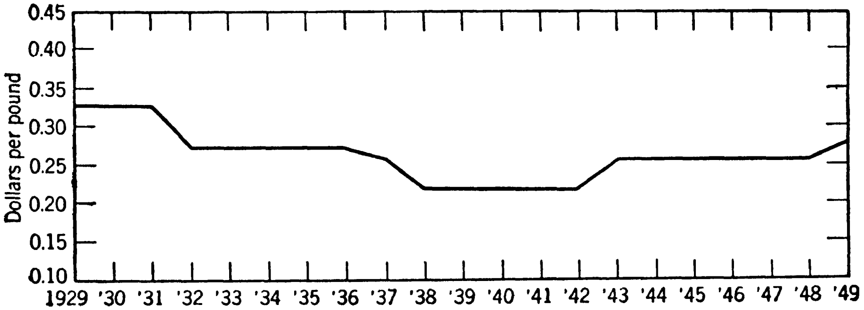
The nitrocellulose used in explosives has a nitrogen content above 12.2 per cent. Although the theoretical nitrogen content of cellulose trinitrate, $[C_6H_7O_2(NO_3)_3]_x$, is 14.14 per cent, the upper nitrogen limit obtainable in practice is about 13.8 per cent. Pyrocotton contains about 12.6 per cent nitrogen, whereas the products containing more than 13.2 per cent are known as guncottons. Smokeless powder generally contains approximately 13.15 per cent nitrogen and is made by blending pyro- and guncotton.



Production—Cellulose Nitrate (Excluding military explosives)

Use Pattern

	Per cent
Plastics, lacquers, and films	90
Explosives	10
	100



Price—Cellulose Nitrate

Miscellaneous

Properties. White solid, moistened with approximately 30 per cent alcohol, in the following types according to solvent required and viscosity of a standard solution:

Special Soluble—SS ¼ sec to 6 sec—10.7 to 11.2 per cent nitrogen. Almost completely soluble in ethyl alcohol alone and completely soluble in combinations of alcohol and aromatic hydrocarbons such as toluene.

Alcohol-Soluble—AS ½ sec—11.2 to 11.7 per cent nitrogen. Soluble in same solvents as RS type, except alcohols are more suitable than hydrocarbons as diluents.

Regular Soluble—RS ¼ sec to 1,000 sec—11.8 to 12.2 per cent nitrogen. Also RS 10 to 15 cp (0.03 sec). Most widely used in lacquers, it is soluble in esters (acetates), ketones, and mixtures of ester and alcohol. Solutions tolerate considerable dilution with toluene and petroleum hydrocarbons.

Plastic or Celluloid—10.8 to 11.5 per cent nitrogen—in form of molding powders, sheets, rods, and tubes prepared from a mixture of cellulose nitrate, alcohol, and plasticizer (such as camphor).

Grades.

	Nitrogen content, per cent
Celluloid (plastic)	10.8 11.5
Soluble (collodion, lacquer)	11.8-12.2
Pyrocotton	12.4-12.8
Guncotton	13.3 13.8

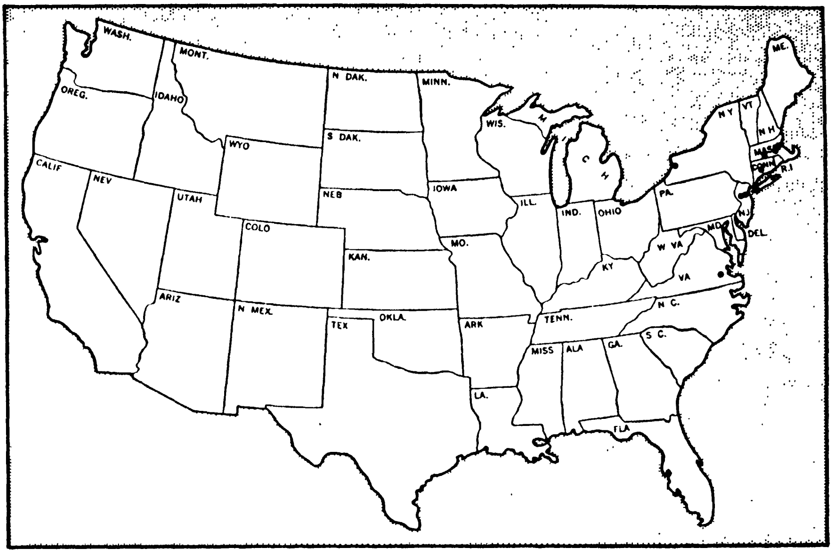
Containers and Regulations. Soluble cellulose nitrate in galvanized steel barrels and smaller containers with alcohol. Red ICC shipping label required.

Economic Aspects

Cellulose nitrate, commonly called "nitrocellulose," found its first use as guncotton and later became the initiating and principal factor in the rayon, lacquer, film, and plastics industries. Because of its flammability it was displaced in the rayon industry by viscose and cellulose acetate, in the lacquer industry partially and in the film industry almost completely by cellulose acetate, and in the plastics industry partially by a wide variety of synthetic resins. Accordingly, the smokeless-powder field, and only part of the lacquer and plastics field, remain as markets for cellulose nitrate. In 1947 cellulose nitrate accounted for only 13 per cent of total cellulosic derivative production.

In wartime, production for smokeless powder naturally increased markedly. The peacetime industry makes both "guncotton" and the lower nitrated lacquer constituent. The manufacturing operation is hazardous, both from explosive and fire standpoints.

A number of smokeless-powder plants were built during the past war. Most of them contained complete facilities for manufacture of the various acids and other materials involved in smokeless-powder production. Accordingly, their cost was not indicative of the cost of a normal cellulose nitrate plant.

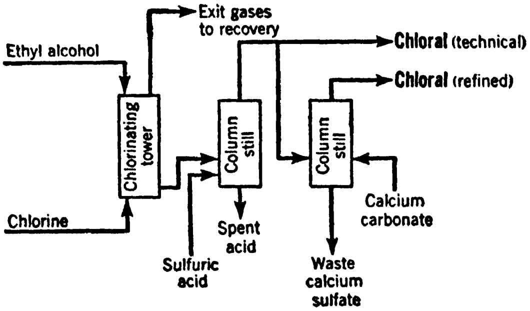


Location of Nitrocellulose Plants

CHLORAL

CCl_3CHO

From Ethyl Alcohol by Chlorination



Reaction

$$C_2H_5OH + Cl_2 \longrightarrow C_2H_5OCl + HCl$$

$$CH_3CH_2OCl + C_2H_5OH \longrightarrow CH_3CH(OH)OC_2H_5 + HCl$$

$$CH_3CH(OH)OC_2H_5 + 3Cl_2 \longrightarrow CCl_3CH(OH)OC_2H_5 + 3HCl$$

$$CCl_3CH(OH)OC_2H_5 \xrightarrow{H_2SO_4} CCl_3CHO + C_2H_5OH$$

83% yield

Material Requirements

Basis—1 ton chloral (technical)

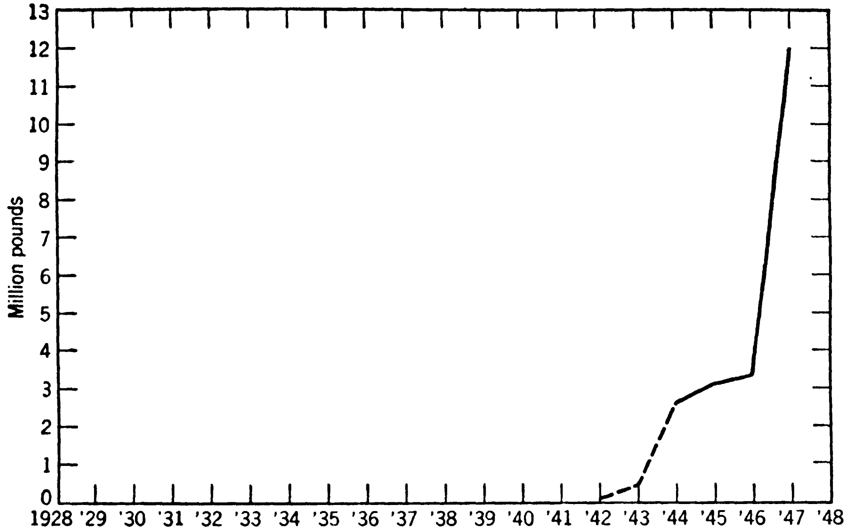
Ethyl alcohol	1,600 lb
Chlorine	5,300 lb
Sulfuric acid (85%) (no recovery)	4,000 lb

Process

Chloral is produced by the liquid-phase chlorination of ethyl alcohol, acetaldehyde, or a mixture of the two. Ethyl chloride is obtained as a by-product in amounts depending on the quantity of water present.

A steel chlorinating tower lined with glazed tile, its height about five times its diameter, is two thirds filled with 95 per cent ethyl alcohol.

Chlorine gas is passed into the bottom of the reactor so that it bubbles up through the alcohol. The initial temperature of the alcohol (20 to 22°C) rises rapidly because of the exothermic reaction and the heat of solution of the liberated hydrogen chloride. The space velocity (volume of chlorine gas at STP divided by the liquid volume of the alcohol) is reduced from about 90 (initial) to 25 as soon as the alcohol reaches reflux temperature. This time is about 2 hr but is generally shortened by using external heating so that hazardous accumulations of ethyl hypochlorite (formed at lower temperatures and immediately decomposed at higher temperatures) are avoided. The temperature is maintained between 78 and 95°C for 20 to 25 hr. During this time the molal ratio of chlorine to alcohol introduced is about 2.25 to 1. The loss of chlorine is negligible through most of the reaction but increases rapidly after the theoretical quantity has been charged (2 moles per mole of ethyl alcohol). About 5 per cent of the chlorine remains unreacted and is found in the exit gases. About 0.15 moles of ethyl chloride per mole of alcohol is formed and may be recovered from the exit gases.



Production—Chloral

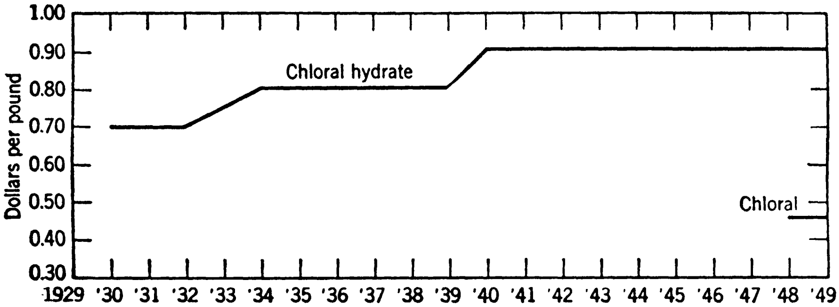
At the end of the chlorination, the clear, yellow, viscous, oily reaction product, which consists of a mixture of chloral hydrate and chloral hemiacetal, is run into a glass-lined still. Here it is mixed with an equal volume of 80 to 85 per cent sulfuric acid, which decomposes the acetal. The mixture is distilled, and the fraction boiling between 93 and 98°C is taken as the chloral cut. The forerunnings (between 70 and 90°C) consist of ethyl alcohol, which may be re-used.

The chloral cut, which consists of a mixture of chloral and chloral hydrate, is classified as crude or technical chloral and may be used directly for the manufacture of DDT.

Refined chloral is produced by redistilling the crude material in the presence of calcium carbonate (to remove acid) and fractionating (97 to 98°C) in a plate column. The yield of chloral is about 83 per cent based on ethyl alcohol. Refined chloral hydrate may be formed by the cautious addition of the requisite amount of water.

Use Pattern

	Per cent
DDT	99
Other (including drugs)	1
	100



Price—Chloral

Miscellaneous

Properties. *Chloral.* Colorless, oily liquid with a penetrating odor. Volatilizes on exposure to air.

Mol. wt.	147.40	M.P.	−57.5°C
Sp. gr.	1.505 25°C/4	B.P.	97.7°C

Soluble in alcohol, ether, and chloroform. Combines with water to form chloral hydrate.

Grades. Technical and USP.

Containers and Regulations. Tank cars, iron drums, and bottles. Poison (Class B) ICC shipping label required.

Properties. *Chloral Hydrate* [$CCl_3CH(OH)_2$]. Transparent, colorless crystals with a pungent odor.

Mol. wt.	165.42	M.P.	57°C
Sp. gr.	1.619 50°C/4	B.P.	97.5°C, decomposes

Soluble in water (474 g per 100 g at 17°C), alcohol, ether, and chloroform.

Grades. Technical and USP.

Containers and Regulations. Paraffined drums, jars, and bottles. No ICC shipping label required.

Economic Aspects

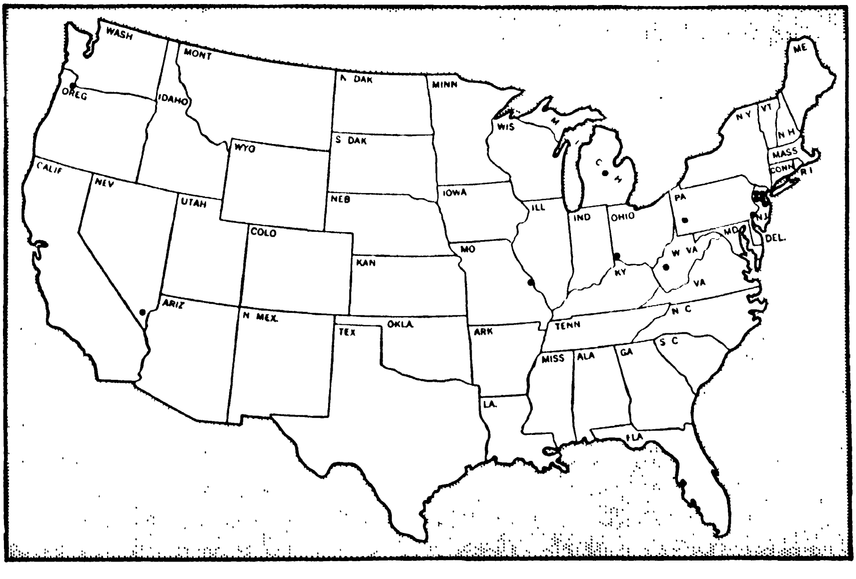
Until 1944 and the advent of DDT into the war program, chloral hydrate was limited in use to the medicinal field and known to the public through detective fiction as "knockout drops." Chloral as such was not listed on the market. The demand for DDT changed this picture, and numerous facilities were built for chloral production, usually at the site of DDT manufacture. This is not necessary, and probably the most economic plant operation can be obtained near a source of chlorine.

Plants built during the war used a modification of the established process for chloral hydrate manufacture. The old chloral hydrate process was a batch affair, but present processes operate in a more nearly continuous manner at higher chlorination temperatures. The early stages of chlorination are critical, and care must be taken to avoid a buildup of explosive hypochlorites.

Glass-lined and structural carbon equipment is generally used because of the corrosiveness of the reactants and products.

One manufacturer employs acetaldehyde as a raw material rather than ethyl alcohol. Essentially the same process is used as with alcohol.

Future use of chloral is directly related to the demand for DDT (see *DDT*).

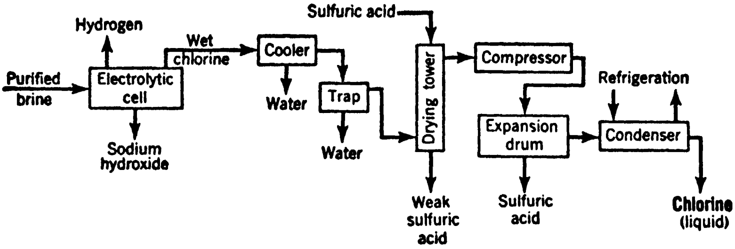


Location of Chloral Plants

CHLORINE

Cl_2

From Salt by Electrolysis



Reaction

$$2NaCl + 2H_2O \xrightarrow[\text{current}]{\text{Direct}} Cl_2 + 2NaOH + H_2$$

95–97% current efficiency

Material and Utility Requirements

Basis—1 ton chlorine plus 2,285 lb sodium hydroxide
plus 10,000 cu ft (57 lb) hydrogen

Salt	3,660 lb	Steam	22,850 lb
Sodium carbonate (58%)	57 lb	Electricity	2,860 kw-hr
Sulfuric acid (66°Bé)	228 lb	Refrigeration	2,060 lb

Process

In the electrolysis of salt, chlorine is produced as a coproduct with sodium hydroxide. Hydrogen is also obtained as a by-product. For process details on cell operation, see *Sodium Hydroxide.*

From the anodes of the electrolytic cells, hot chlorine gas containing considerable water vapor is evolved. It is sent to specially constructed coolers where the temperature of the gas is reduced to 12 to 14°C, just high enough to avoid the formation of solid chlorine hydrate, thereby circumventing the possible plugging of pipes. Most of the water vapor condenses in these coolers, which are usually of the following types:

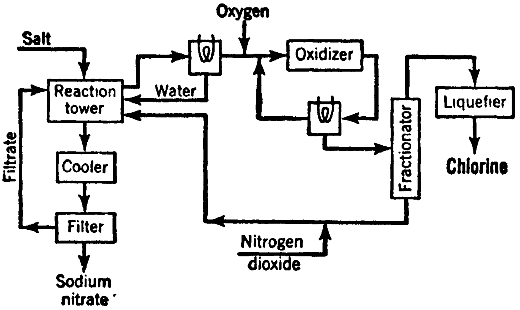
chemical stoneware chlorine lines submerged in water in trenches, water-cooled glass pipes and rubber-lined steel pipes, or stoneware disk coolers. Refrigeration is sometimes used, depending on the available water temperature.

The partially dried chlorine gas is then passed to drying towers where the remaining water is removed by scrubbing with 66°Bé sulfuric acid. After drying, the chlorine can be handled in iron or steel equipment, whereas the extremely corrosive moist chlorine necessitates chemical stoneware, glass, or rubber-lined pipes. The dried gas goes to compressors, which almost invariably are the means of creating a partial vacuum that withdraws the chlorine from the electrolytic cells. Most plants employ only one of the two common methods of compression: centrifugal compressors of the Nash hydroturbine type, which are constructed of iron and have concentrated sulfuric acid as the sealing liquid. These operate at a moderate pressure ranging from 15 to 35 psi gage. The other method compresses chlorine gas to 75 to 80 psi, using various types of sulfuric-acid-sealed reciprocating compressors. The heat of compression is removed progressively with water and refrigeration. A temperature between −30 and −45°C is attained, using single-stage or multiple-stage refrigeration, depending on the amount of compression. Ammonia, carbon dioxide, and "Freon" are commonly employed refrigerants. The resulting liquid chlorine is stored and filled into cylinders or into 30 or 55 ton tank cars.

Some residual (less compressible) gas called "blow gas," an equilibrium mixture of air and chlorine, is usually formed and vented for use in making derivatives such as bleaching powder. The commercial liquid chlorine as produced assays higher than 99.5 per cent. For chlorine that is to be relatively free of nonvolatile material (chlorine content better than 99.9 per cent), a purification procedure may be used. One company passes the chlorine to be liquefied through a bubble-cap column countercurrent to liquid chlorine.

In the manufacture of caustic potash by the electrolysis of potassium chloride, chlorine is produced along with hydrogen. The afore-mentioned recovery process is used, and the electrolysis is carried out under conditions similar to those used on salt. Chlorine is also obtained commercially as a coproduct in the manufacture of magnesium from magnesium chloride and sodium from fused salt. For further information, see *Sodium.*

From Salt and Nitric Acid



Reaction

$$3NaCl + 4HNO_3 \rightarrow Cl_2 + 3NaNO_3 + NOCl + 2H_2O$$

$$2NOCl + O_2 \rightleftarrows Cl_2 + 2NO_2$$

$$3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO$$

$$2NO + Cl_2 \rightleftarrows 2NOCl$$

$$2NaCl + 4NO_2 \rightarrow 2NaNO_3 + 2NOCl$$

Material Requirements (Theoretical)

Basis—1 ton chlorine plus 4,700 lb sodium nitrate

Salt	3,300 lb
Nitric acid (as 100%)	3,550 lb
Oxygen	600 lb

Process

In the nitrosyl chloride process, chlorine and sodium nitrate are produced by treating salt with nitric acid.

Salt is charged into a reaction tower where it is treated with 40 to 70 per cent nitric acid at a temperature of about 60°C. At the high nitric-acid concentration, chlorine gas is obtained directly along with nitrosyl chloride in a ratio of about 2 to 1. With dilute nitric acid (40 per cent), a greater concentration of nitrosyl chloride is formed, but no hydrogen chloride is evolved.

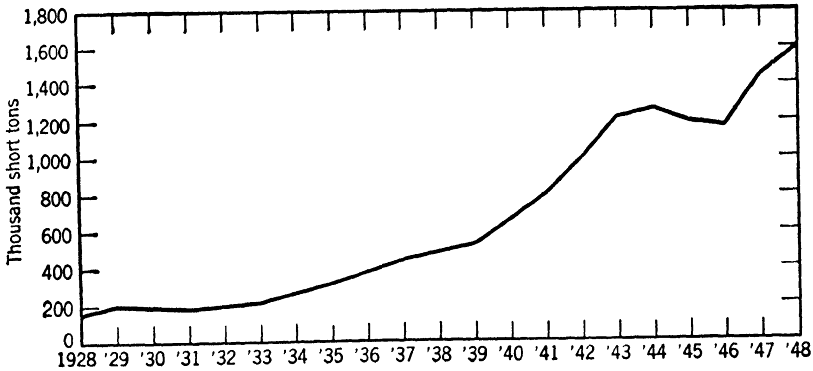
The solution from the reactor is discharged into a cooler where at a temperature of about 30°C sodium nitrate crystallizes. The sodium nitrate is filtered off, dried, and stored for packaging. The filtrate is returned to the reaction tower.

The gases evolved from the reactor (using dilute nitric acid) consist mostly of nitrosyl chloride and are passed through a condenser. Here they are dried by cooling to about 0°C, and the condensed moisture is returned to the reactor. Until this step it is necessary to handle the extremely corrosive gases and solutions in chemical stoneware or similar ceramic materials. The dried gas, now containing less than 0.1 per cent water vapor, may be handled in nickel and its alloys. It is mixed with oxygen in a 2-to-1 ratio and passed through an oxidizer. By using a contact catalyst such as zeolite (aluminum silicate) or aluminum oxide at a temperature of 300 to 400°C and a pressure of about 120 psi, nitrosyl chloride is oxidized in the vapor phase to chlorine and nitrogen dioxide.

Liquid-phase oxidation may be employed by passing oxygen through liquefied nitrosyl chloride at 60°C and a pressure of 400 psi; hot nitric acid may be used in place of oxygen.

The gaseous products from the oxidizer are liquefied in a condenser at −50°C where the oxygen is separated and recirculated to the oxidizer. The liquid is pumped into a fractionator from which chlorine gas is taken overhead and liquefied in the usual manner.

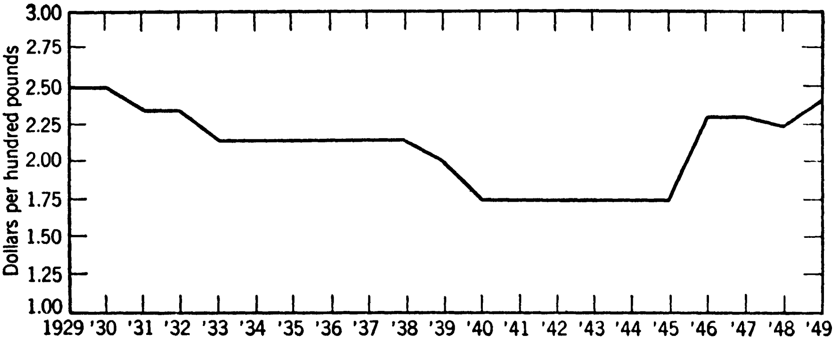
Nitrogen compounds including nitrogen dioxide and about 25 per cent by weight of unoxidized nitrosyl chloride are removed from the bottom of the fractionating tower, vaporized, mixed with additional nitrogen dioxide (from an ammonia oxidation unit), and passed into the reaction tower to produce additional nitric acid to start the process. The many side reactions, which yield various lower oxides of nitrogen, must be controlled, and the existence of these reactions makes the process quite complicated. Besides chlorine and sodium nitrate, nitrosyl chloride may be obtained as an end product.



Production—Chlorine

Use Pattern

	1948 (est.), per cent
Pulp and paper processing	20
Chlorobenzenes	12
Cleaning fluids and refrigerants	18
Chlorinated ethylene products (other than cleaning fluids)	10
Other chemicals	20
Disinfectants and sanitation	5
Textiles	5
Miscellaneous	10
	100



Price—Chlorine

Miscellaneous

Properties. Heavy, toxic greenish-yellow gas with a pungent, irritating odor, which may be compressed to a yellowish liquid at 15°C under a pressure of 5.7 atm or −33.6°C under atmospheric pressure.

Mol. wt.	70.91	M.P.	−101.6°C
Sp. gr.		B.P.	−34.6°C
Gas	2.49 (0°C—air = 1)		
Liquid	1.56(−33.6°C)		

Liquefaction point 6.8 atm (room temperature) or −40°C (760 mm)
Critical temperature 146°C Critical pressure 93.5 atm

Weight per cu ft	0.201 lb (gas) 91.70 lb (liquid)

Liquid chlorine is soluble in water (1.46 per cent at 0°C, 0.57 per cent at 30°C), and alkalies. Chlorine gas is soluble in water to the extent of 310 cc per 100 g at 10°C and 177 cc per 100 g at 30°C.

Grades. Technical (99.9 per cent).

Containers and Regulations. Tank cars, multiple-unit cars, and steel cylinders. Chlorine gas and vapors are poisonous. Green (gas) ICC shipping label required.

Economic Aspects

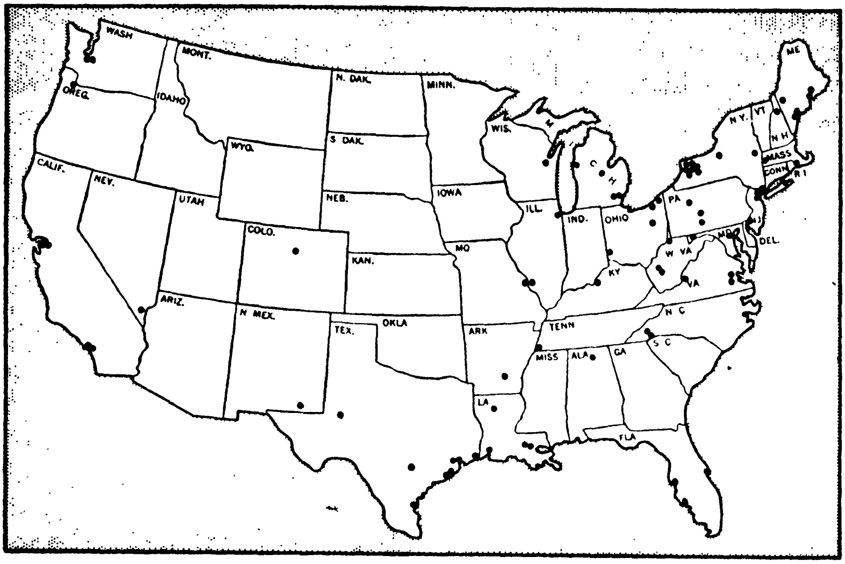
Electrolytic chlorine and its coproduct, caustic soda, have nearly as wide distribution in industry as does sulfuric acid. Chlorine is particularly important to the synthetic-organic-chemical industry, and future increases in requirements will undoubtedly stem from increased demand for synthetic organic chemicals. As demand increases, more plants will probably be built by chlorine consumers if recent trends mean anything. In 1939, 34 per cent of the chlorine produced was consumed in the producing plant, whereas the comparable figure for 1947 was 64 per cent.

It is obvious, of course, that demand for the joint product, caustic soda, must be sufficient for profitable sale if chlorine is to be produced economically. Accordingly, considerable thought is being given to the development of nonelectrolytic processes, including modernization of the old Deacon and Weldon processes. Other possibilities are the reaction of sulfur trioxide with salt to produce chlorine and sulfur dioxide, the decomposition of chlorosulfonic acid, and the oxidation of hydrochloric acid. Further developments in the production of cheap tonnage oxygen will make the last-named process attractive, if corrosion problems can be overcome. A complete plant (including acid and oxygen facilities), making 100 tons chlorine per day from salt and sulfuric acid, will cost in the neighborhood of $3,000,000.

Recent expansion in chlorine production has been by means of diaphragm cells, which produce relatively impure caustic soda. Several processes have been developed for purification of diaphragm-cell liquors, but these add somewhat to production cost. Considerable interest has been shown in the vertical rotating cathode mercury cell developed in Germany during World War II, which yields pure caustic-soda liquors. An American mercury cell has also recently been developed (see *Sodium Hydroxide*).

Competition within the electrolytic chlorine industry centers around the type of cell used. Most recent plants have installed Hooker S cells, although the Hooker-Columbia cell, the Dow bipolar cell, and the Vorce cell, a cylindrical cell, are still popular. About 20 other types of cells are used by various producers. Important competitive factors are cell cost, space requirements, current and voltage efficiencies, power efficiency, anode and diaphragm life, caustic concentration, and purity. Typical operating performance of a 5,000-ampere Hooker S cell is as follows: Voltage, 3.28; effluent temperature, 85°C; NaOH concentration, 135 gpl; $NaClO_3$–NaOH ratio, 2.5 parts per thousand; current efficiency, 94 per cent; voltage efficiency, 70 per cent; power efficiency, 66 per cent; anode life, 660 days; diaphragm life, 220 days; NaOH per cell per day, 373 lb, equivalent to 5.3 lb per sq ft of floor space; chlorine per cell per day, 330 lb, equivalent to 4.7 lb per sq ft of floor space. Recent installations are slightly more efficient.

In the past, electrolytic plants have been built in units of 50 tons of chlorine per day. The largest known single unit is a Hooker S cell installation with a capacity of 300 tons of chlorine per day. Other installations are as small as 3 to 5 tons daily. In 1945 more than 70 per cent of installed chlorine capacity consisted of diaphragm cells.



Location of Chlorine Plants

Because of the large amount of electricity required, a common decision that is necessary is whether to purchase or manufacture power. At one time cheap power and cheap salt were the main factors in locating electrolytic chlorine plants, but recently transportation costs have led to the location of plants near the product market, despite higher power and salt costs. Disposal of by-product hydrogen varies from one plant to another. Some plants waste it; others use it as fuel. Efforts at utilization in the manufacture of ammonia, hydrogen chloride, and methanol have also been made from time to time.

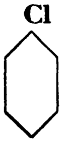
Between 10 and 15 per cent of the total chlorine marketed is produced from sources other than the electrolytic caustic–chlorine process. These include the nitrosyl chloride process (1 to 2 per cent) and by-product chlorine from the electrolytic production of caustic potash (1 to 2 per cent) and from magnesium and metallic sodium (8 to 10 per cent).

To avoid the by-product problem, numerous attempts have been made to develop methods of producing chlorine from hydrochloric acid. During World War II, German scientists developed an electrolytic cell for this purpose at Wolfen. This was a series-type cell, with bipolar graphite electrodes, built like a filter press and had a daily capacity of one ton of chlorine. The nitrosyl chloride process presents a problem similar to that of electrolytic chlorine in that by-product sodium nitrate requires profitable disposal.

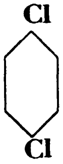
A 100-ton-per-day electrolytic plant complete with caustic-soda facilities costs about $8,000,000. The lone nitrosyl chloride plant is said to have a capacity of 55 tons per day.

Among the new uses for chlorine, which may be expected to increase demand greatly in the future, are the silicones, certain of the synthetic rubbers, and an expanded vinyl chloride industry. On the other hand, certain losses in use have already appeared. Examples are replacement by peroxides for bleaching textiles, and new acetic anhydride processes replacing the old sulfur chloride process. In the over-all picture, however, more gains are promised than losses.

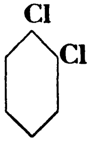
CHLOROBENZENE
DICHLOROBENZENE



Mono-
Chlorobenzene



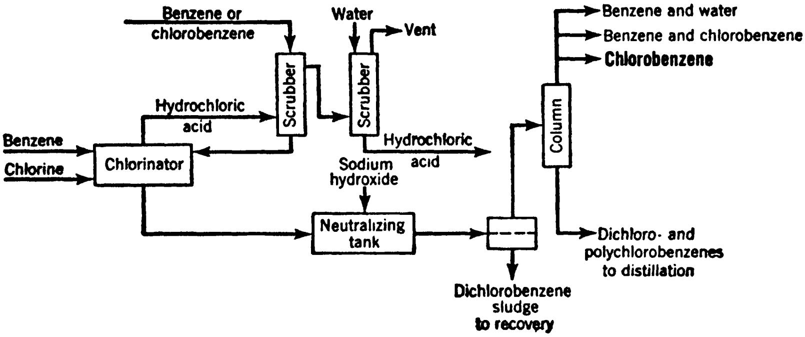
Para-



Ortho-

Dichlorobenzene

From Benzene and Chlorine



Reaction

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$

$$C_6H_5Cl + Cl_2 \rightarrow C_6H_4Cl_2 + HCl$$

70–75% yield (monochlorobenzene)

20–10% yield (dichlorobenzene)

Material Requirements

Basis—1 ton chlorobenzene

Benzene	1,900 lb
Chlorine	1,750 lb
Iron turnings	Small

Process

Batch. Dry benzene is charged into a tall cast-iron or steel tank (chlorinator) lined with lead or glass. About 1 per cent by weight (of the benzene charge) of iron turnings is used as the catalyst and remains in the chlorinator after each batch. Chlorine is bubbled into the charge at a rate to keep the temperature at 40 to 60°C. The chlorination is continued until the proper density is reached. When only monochlorobenzene is desired, the chlorination temperature is maintained at about 40°C, and about 60 per cent of the theoretical chlorine is used. When all the benzene is chlorinated, the reaction is run at the higher temperature (55 to 60°C), and a density of 1.280 (15°C) is reached in about 6 hr.

The hydrogen chloride given off during the reaction is scrubbed with benzene or chlorobenzene to remove organic spray and is absorbed in water in a suitable absorption system to give hydrochloric acid.

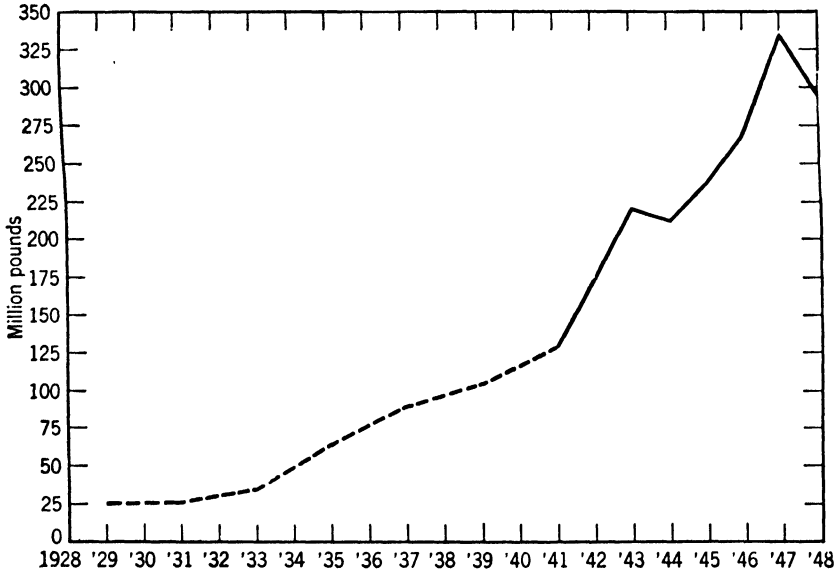
The chlorinated benzene is delivered to the neutralizer (a jacketed steel tank equipped with a reflux condenser and vent) containing an aqueous solution (10 per cent) of caustic soda. The charge is thoroughly agitated to insure neutrality and is kept warm by jacketed steam. The faintly alkaline chlorinated benzene is allowed to settle in the separator. A sludge rich in dichlorobenzenes settles out and is withdrawn at the bottom for distillation. The bulk of the material is distilled and separated into several fractions. If the chlorination is carried out so that the theoretical quantity of chlorine is consumed (100 per cent chlorination), the following fractions are obtained in approximately the indicated percentages:

	Per cent
Benzene and water	3
Benzene and chlorobenzene	10
Chlorobenzene	75
Chlorobenzene and dichlorobenzenes	10
Resinous materials and loss	2

The first two fractions are returned to the system for further processing, and the third (chlorobenzene) is run to storage. The fourth fraction is allowed to accumulate and is then distilled. The para isomer is collected in the distillate; the residue contains the ortho isomer contaminated with some para isomer and polychlorobenzenes, principally 1,2,4-trichlorobenzene. Of the two isomeric dichlorobenzenes (practically no meta isomer formed), the para compound is formed in the larger quantity; the ratio of para to ortho is approximately 8 to 1. The composition of the chlorinated products varies according to the chlorination temperature, rate, degree, and catalyst. However, a 100 per cent chlorination will yield approximately the following composition: chlorobenzene, 80 per cent; *p*-dichlorobenzene, 17 per cent, and *o*-dichlorobenzene including polychlorobenzenes, 3 per cent.

Continuous. When monochlorobenzene is desired with the formation of a minimum amount of higher chlorinated products, a combination chlorination and fractionation apparatus may be used. In this manner, the monochlorobenzene is isolated as quickly as it is formed, and only fresh benzene is exposed to the chlorine. Benzene is charged simultaneously into a chlorinator and fractionating chamber. The benzene in the chlorinator is heated to its boiling point, and chlorine is introduced. The partially chlorinated material runs into the distillation unit, where the benzene is distilled, condensed, and returned to the chlorinator. The monochlorobenzene is withdrawn from the fractionating column and is neutralized and distilled in the manner described in the batch process.

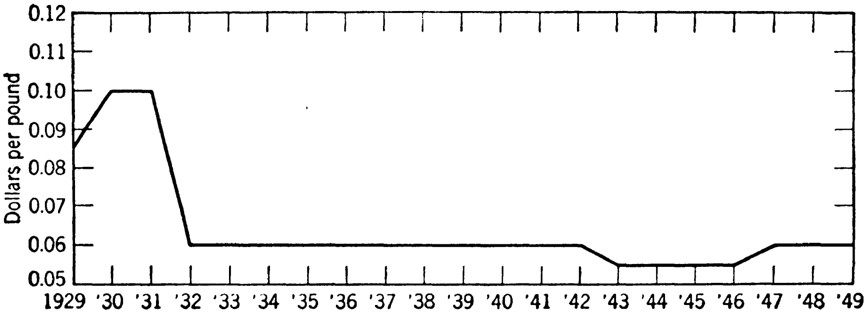
Because of the increasing uses for *p*-dichlorobenzene, its by-product production has been supplemented by its manufacture as a primary product. This is accomplished by chlorinating benzene in the presence of aluminum chloride to give a high yield of *p*-dichlorobenzene.



Production—Chlorobenzene (Mono-)

Use Pattern

	1947 (est.), per cent
Monochlorobenzene	
Phenol	70
Aniline	7
DDT	13
Miscellaneous	10
	100
Dichlorobenzenes	
Moth repellent and deodorant	70
Other	30
	100



Price—Chlorobenzene (Mono-)

Miscellaneous

Properties. *Monochlorobenzene.* Colorless, mobile, volatile liquid possessing an almond-like odor.

Mol. wt.	112.56	M.P.	−45.2°C
Sp. gr.	1.107 20°C/4	B.P.	132.1°C

Weight per gallon 9.19 lb (25°C)

Soluble in alcohol, benzene, chloroform, and ether in all proportions at room temperature. Insoluble in water.

Flash point (closed cup)	85°F
Vapor density (air = 1)	3.88
Explosive limits (% by volume in air)	Lower 1.8 at 212°F Upper 9.6 at 302°F

o-Dichlorobenzene. Colorless, volatile liquid with a pleasant aromatic odor.

Mol. wt.	147.01	M.P.	−17.6°C
Sp. gr.	1.305 20°C/4	B.P.	179°C

Weight per gallon 10.9 lb (25°C)

Soluble in alcohol, benzene, ether, and most organic solvents. Insoluble in water.

Flash point (closed cup)	151°F
Vapor density (air = 1)	5.07

p-Dichlorobenzene. White crystals which are volatile and possess a pleasant, penetrating odor.

Mol. wt.	147.01	M.P.	53°C
Sp. gr.	1.458 (21°C)	B.P.	173.7°C

Soluble in alcohol, ether, benzene, chloroform, and carbon disulfide. Insoluble in water.

Flash point (closed cup)	150°F
Vapor density (air = 1)	5.07

Grades. Monochlorobenzene: technical. Orthodichlorobenzene: technical (85 to 88 per cent *o*-dichlorobenzene with varying amounts of *p*-dichlorobenzene and trichlorobenzene), and purified (95 to 96 per cent with not over 4 per cent *p*-dichlorobenzene and trichlorobenzene). Paradichlorobenzene: technical.

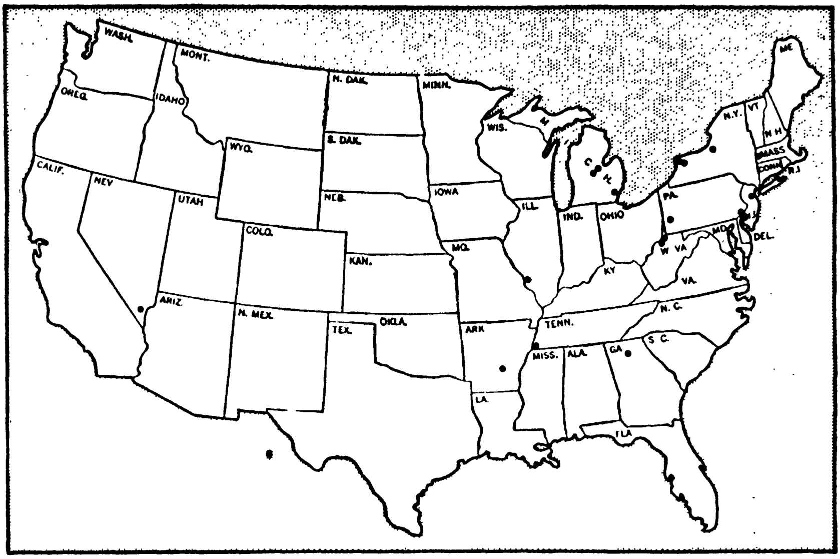
Containers and Regulations. Monochlorobenzene and *o*-dichlorobenzene: tank cars, drums, and bottles. Paradichlorobenzene: steel barrels, drums, tins, cans, and bottles. No ICC shipping label required on mono- or dichlorobenzenes.

Economic Aspects

Demand for monochlorobenzene comes practically entirely from the synthetic-organic-chemical industry. Accordingly, since the manufacturing process is simple, it is often manufactured in the same plant in which it is consumed. Where only comparatively small amounts are required, it is often cheaper to buy it from a producer of a general line of chemicals of this type. In either case, by-product ortho- and paradichlorobenzenes must be disposed of by the producer.

Most of the monochlorobenzene produced in the past has been used in the manufacture of phenol and aniline. The only large new use of recent years has been in DDT manufacture. The chief demand for *p*-dichlorobenzene has been as a moth repellent, in which field it is gradually replacing naphthalene (moth balls).

Quantities as low as 1,000,000 lb monochlorobenzene annually may be made economically, although most plants are considerably larger.



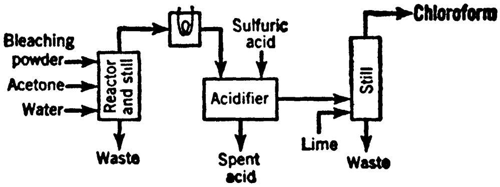
Location of Chlorobenzene Plants

CHLOROFORM

(TRICHLOROMETHANE)

$CHCl_3$

From Acetone and Bleaching Powder



Reaction

$$2CH_3COCH_3 + 6CaOCl_2 \cdot H_2O \rightarrow 2CHCl_3 + (CH_3COO)_2Ca + 2Ca(OH)_2 + 3CaCl_2 + 6H_2O$$

88% yield

Material Requirements

Basis—1 ton chloroform

Acetone	1,100 lb	Lime	Small
Bleaching powder	12,500 lb	Water (process)	4,750 gal
Sulfuric acid (concentrated)	1,150 lb		

Process

The action of bleaching powder ($CaOCl_2 \cdot H_2O$) on acetone, acetaldehyde, or ethyl alcohol yields crude chloroform, which may readily be purified by chemical treatment and distillation.

In the older, more common batch process, water is run into a mixing tank. Using good agitation, bleaching powder containing about 34 per cent available chlorine is slowly charged to the mixer in the ratio of about 3 lb per gal of water. The suspension of bleaching powder in water is strained into a cast-iron still, fitted with efficient agitation, cooling coils, and heating coils.

Acetone is slowly run into the still (approximately 0.1 lb of acetone per lb of bleaching powder), and the temperature is maintained below 110°F by the cooling coils and rate of addition. When all the acetone has been added, the pot temperature is raised to 134°F where chloroform begins to distil. By gradually increasing the temperature to 150°F, practically all the chloroform formed is distilled over.

The vapors are passed through a condenser and collected in a tank fitted with an agitator. The crude material (crude chloroform and water) is purified by agitation with concentrated sulfuric acid in a weight ratio of about 2 lb of crude chloroform (distillate) per lb of sulfuric acid. After 2 to 3 hr agitation the crude chloroform (which does not impart any color to clear concentrated sulfuric acid) is decanted from the acid and charged to a still, where it is distilled over calcium oxide (lime).

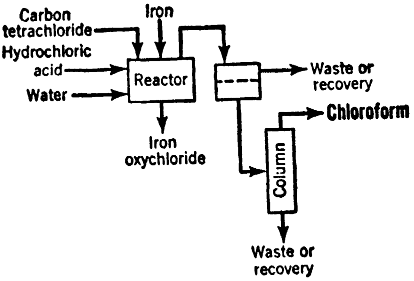
The purified chloroform assays over 99 per cent and is obtained in an 86 to 91 per cent yield based on the acetone charged.

A yield of 80 per cent of chloroform may be realized using acetaldehyde. A 20 per cent aqueous solution of acetaldehyde is charged into a solution of bleaching powder containing 9 to 10 per cent active chlorine. After vigorous stirring of the solution maintained at 110 to 115°F, the product is neutralized, and chloroform is separated by distillation and purified as described previously.

These processes may be run on a continuous basis and also may utilize a mixture of acetone and acetaldehyde as the raw material.

Industrial ethyl alcohol has been used to make chloroform and was the basis for the original bleaching-powder process. By employing a method similar to those described previously, 1 ton of chloroform is produced from 19,400 lb of bleaching powder (35 per cent available chlorine), 225 gal of 95 per cent alcohol, and about 40 tons of steam.

From Carbon Tetrachloride by Reduction



Reaction

$$CCl_4 + 2(H) \xrightarrow[H_2O]{Fe} CHCl_3 + HCl$$

70–80% yield

Material Requirements

Carbon tetrachloride	3,450 lb
Iron	2,750 lb
Hydrochloric acid (22°Bé)	3.5 lb

Process

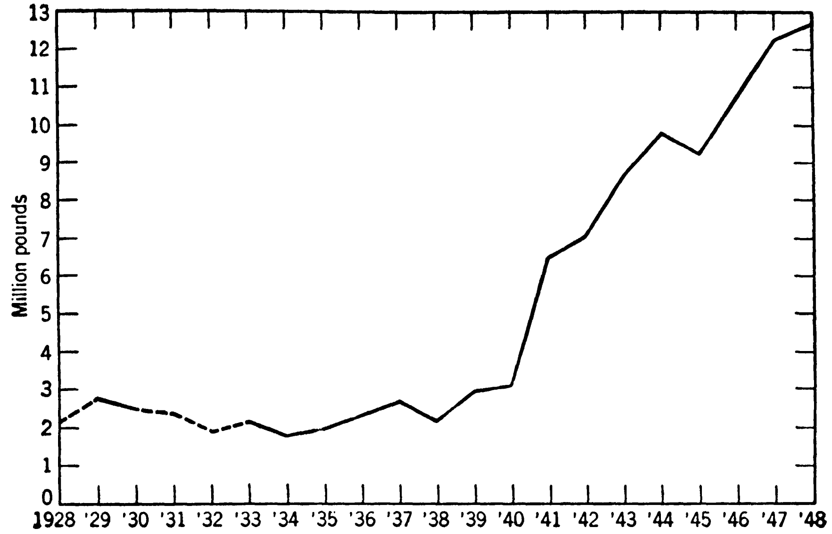
The reduction of carbon tetrachloride using moist iron and hydrochloric acid as the source of hydrogen yields chloroform.

Carbon tetrachloride is charged into an iron kettle fitted with an efficient agitator. About 0.1 per cent of concentrated hydrochloric acid (based on the weight of carbon tetrachloride) and water (4 lb for every 5 lb of carbon tetrachloride) are added with mixing. Iron is slowly charged to the agitating mixture until a weight equal to that of the water has been added. Stirring is continued for 40 to 70 hr until the reaction is completed. During this time the temperature of the reactor is maintained at 15°C. A sludge of oxychlorides of iron is formed during the reaction.

The reaction mixture is steam-distilled to give crude chloroform, which is then fractionated to give pure chloroform in a 70 to 80 per cent yield based on carbon tetrachloride.

From Methane by Chlorination

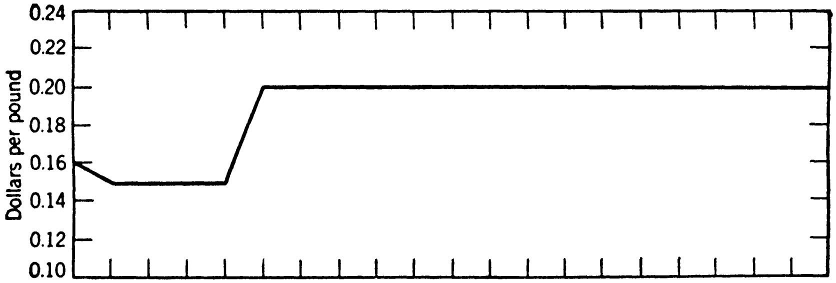
Chloroform may be produced by chlorinating methane in a manner similar to that described for methyl chloride (see *Methyl Chloride*). In fact, the chlorination process may be so varied as to produce a preponderance of any one of the chloromethanes. One method used to obtain chloroform predominantly is to increase the chlorine–methane ratio as shown under *Methyl Chloride*, so that a mixture of methylene chloride–methyl chloride results. This mixture, which may vary from a ratio of 4 volumes of methyl chloride and 2 volumes of methylene chloride to 2 volumes of methyl chloride and 3 volumes of methylene chloride, is passed with one volume of chlorine through a silica-lined reactor heated to 400 to 500°C until all the chlorine has been consumed. The gases are cooled and mixed with more chlorine, so that the volume ratio of total chlorinated hydrocarbons to chlorine is 1 to 2 in both chlorination steps. After passage through a second reactor maintained at the same temperature, the gases contain 15 to 30 per cent chloroform with negligible amounts of carbon tetrachloride. The chloroform is separated, and the lower chlorinated materials are recycled for re-use.



Production—Chloroform (USP and technical)

Use Pattern

Dye manufacture Drugs and pharmaceuticals Solvent	No breakdown available



Price—Chloroform

Miscellaneous

Properties. Colorless, highly refractive, nonflammable, volatile liquid with a characteristic odor.

Mol. wt.	119.39	M.P.	−63.5°C
Sp. gr.	1.489 (20°C)	B.P.	61.2°C

Weight per gallon 12.4 lb (20°C)

Soluble in alcohol, ether, benzene, and petroleum ether. Slightly soluble in water (0.82 per cent at 20°C).

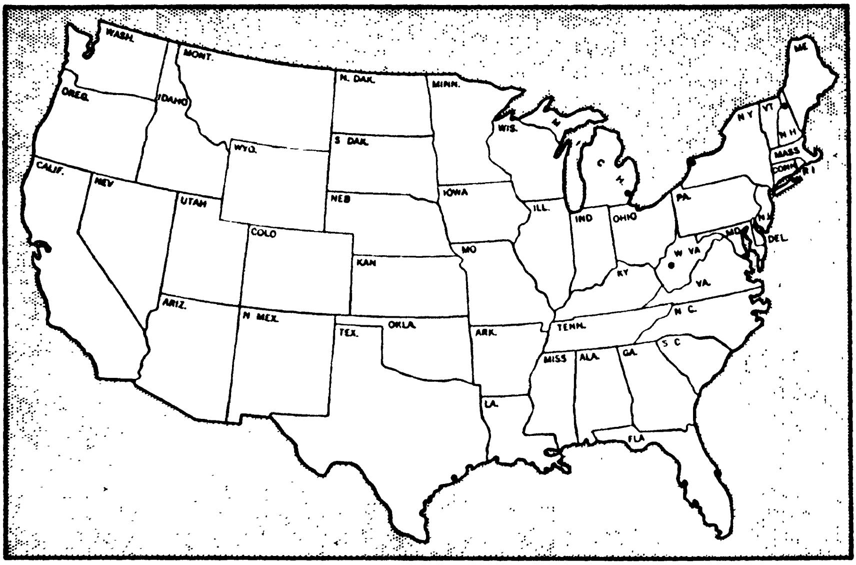
Flash point (closed cup)	Nonflammable
Vapor density (air = 1)	4.13

Grades. Technical, USP, and C.P. Anesthetic grade (USP) contains 1 to 2 per cent added ethyl alcohol as stabilizer.

Containers and Regulations. Tank cars, drums, tins, and bottles. No ICC shipping label required.

Economic Aspects

Compared with the production of other chlorinated hydrocarbons, production of chloroform is relatively small. It is usually manufactured by companies making other chlorinated hydrocarbons or to round out a line of other fine chemicals.



Location of Chloroform Plants

The most important process by far is the action of bleaching powder on acetone or ethyl alcohol. The latter is the usual raw material because of ease of handling. A small amount is made by the reduction of carbon tetrachloride by moist iron. It is also possible to electrolyze a 20 per cent sodium chloride solution containing acetone to yield gaseous chloroform, which is evolved from the cell and condensed. Only under very specialized conditions would such a plant be economic. Some chloroform is recovered as a by-product of the chlorination of methane to yield carbon tetrachloride.

Plant costs for the bleaching-powder process are comparatively small; it is estimated that a plant of 5,000,000 lb annual capacity can be built for $90,000.

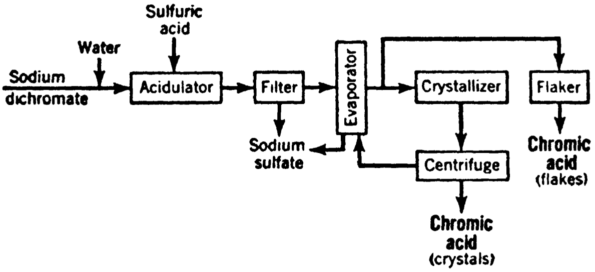
At one time, chloroform was used rather widely as an anesthetic, but this use is decreasing. No other large uses are in prospect, largely because of the danger of anesthesia in handling. The increase in production since 1944 can be attributed largely to its use as an extraction agent in penicillin manufacture.

CHROMIC ACID

(CHROMIUM TRIOXIDE, CHROMIC ANHYDRIDE)

CrO_3

From Sodium Dichromate



Reaction

$$Na_2Cr_2O_7 \cdot 2H_2O + H_2SO_4 \rightarrow 2CrO_3 + Na_2SO_4 + 3H_2O$$

Material Requirements

Basis—1 ton chromic acid

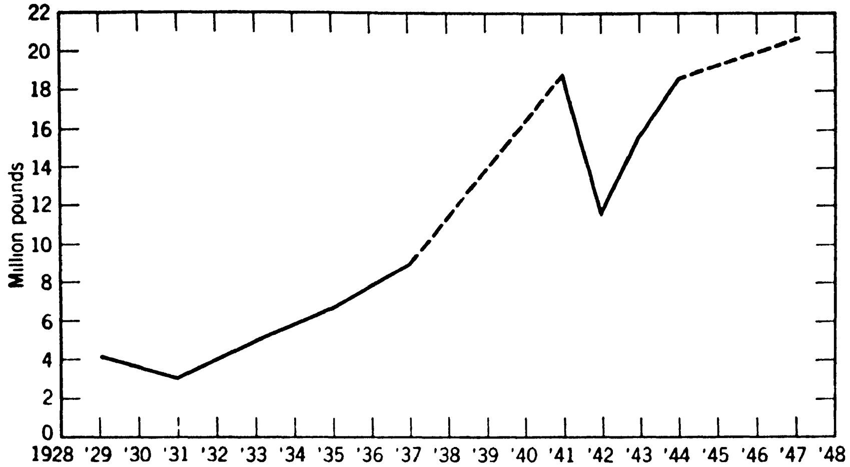
Sodium dichromate dihydrate	3,000 lb
Sulfuric acid (66°Bé)	1,500 lb

Process

Chromium trioxide, or chromic anhydride, CrO_3, which is commercially (though erroneously) called chromic acid, is produced by the action of concentrated sulfuric acid on a solution of chromate or dichromate.

Sodium dichromate and water are charged into an acidulator in a weight ratio of about 3 to 1 at room temperature. Alternately, a saturated solution of sodium dichromate from the evaporator or crystallizer in the dichromate plant (see *Sodium Dichromate*) may be used. Concentrated sulfuric acid (66°Bé) is slowly added to the dichromate solution with cooling and good agitation. Approximately 1 part of sulfuric acid is required for 2 parts of sodium dichromate. The dichromate is converted into chromium trioxide with the resulting formation of sodium sulfate. The latter partially crystallizes out during the acidification.

The reaction product is filtered to remove the precipitated sodium sulfate, and the filtrate is concentrated in evaporators. Any sodium sulfate remaining is crystallized out during evaporation and is discharged from the bottom of the evaporator. The saturated chromic-acid solution is fed into a crystallizer, where red prismatic needles of chromic acid separate on cooling. The cooled slurry is fed to a centrifuge, and the mother liquor is returned to the evaporator. The crystals are dried at a low temperature (below 100°C) to yield technical chromic acid.



Production—Chromic Acid (100%)

The technical product may be purified by recrystallization. Alternately, a saturated solution of the acid may be flaked to yield chromic acid, which assays above 99 per cent CrO_3.

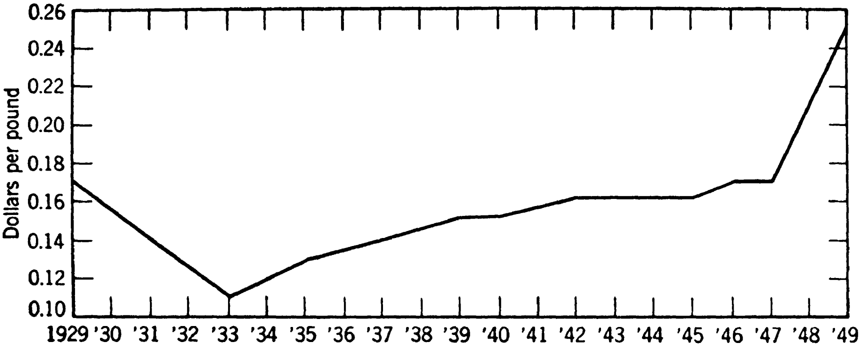
Chromic acid, used as an oxidizing agent in the preparation of organic compounds, may be regenerated by electrolytic oxidation. In the oxidation of organic compounds, chromic acid in a solution of sulfuric acid is reduced and forms chromium sulfate. A typical solution, after oxidation, may contain about 1 part of chromic acid as chromium sulfate and 3.5 parts of sulfuric acid. This solution is electrolyzed between lead electrodes in a lead-lined tank divided by a diaphragm. The anodes become covered with lead oxide while chromic acid is formed in the anolyte.

True chromic acid, H_2CrO_4, is reputed to be formed by heating the anhydride with a small amount of water and cooling. However, if it does exist, it is very unstable and is not isolated commercially. Aqueous solutions of chromium trioxide are strongly acid and are believed to contain several polychromic acids such as dichromic ($H_2Cr_2O_7$) and trichromic acid ($H_2Cr_3O_{10}$), although chromic acid (H_2CrO_4) is also no doubt present.

Use Pattern

Not including manufacture of other primary chromium chemicals

	Per cent
Metal treatment	75
Miscellaneous uses & export	25
	100



Price—Chromic Acid

Miscellaneous

Properties. Deep red to reddish-brown very deliquescent rhombic crystals. Volatilizes at about 110°C.

Mol. wt.	100.01	M.P.	197°C with decomposition
Sp. gr.	2.70		

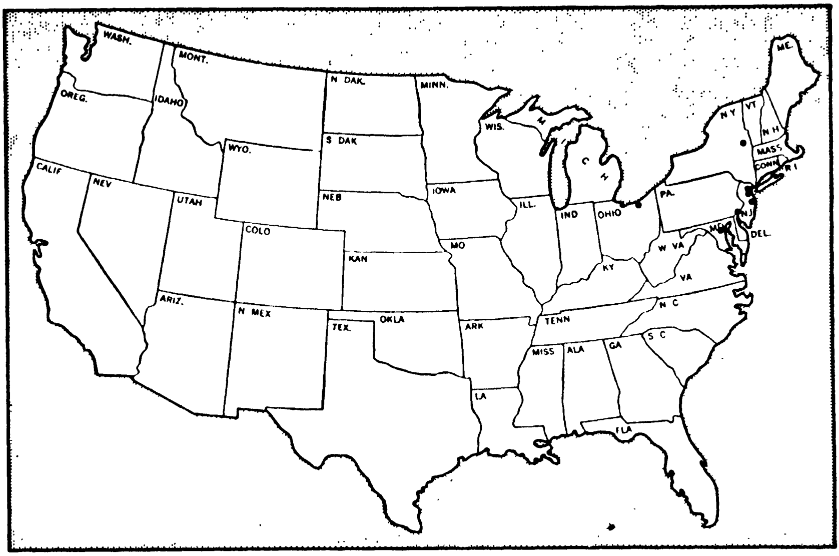
Soluble in water (164.9 g per 100 g at 0°C, 206.7 g per 100 g at 100°C), sulfuric acid, and alcohol. When heated to 250°C, it decomposes into chromic oxide (Cr_2O_3) and oxygen.

Grades. Technical (99.75 per cent), C.P., and USP in crystals and flakes.

Containers and Regulations. Drums, cases, cans, tins, jars, and bottles. It is a very powerful oxidizing agent and should be carefully isolated from organic materials. Alcohol, dropped on chromic acid readily catches fire. Yellow ICC shipping label required.

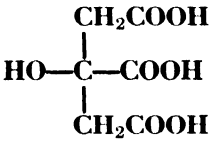
Economic Aspects

Since chromic acid is made from sodium dichromate, it is usually manufactured by producers of the latter. Production in recent years has doubled, chiefly because of demand for metal treatment and corrosion prevention. Even so, production is only a little over 10 per cent of sodium chromate and dichromate production, which salts are the chief source of "primary chromium chemicals." This classification includes, in addition to the afore-mentioned compounds, potassium dichromate and chromate, ammonium dichromate, and chromium tanning compounds.



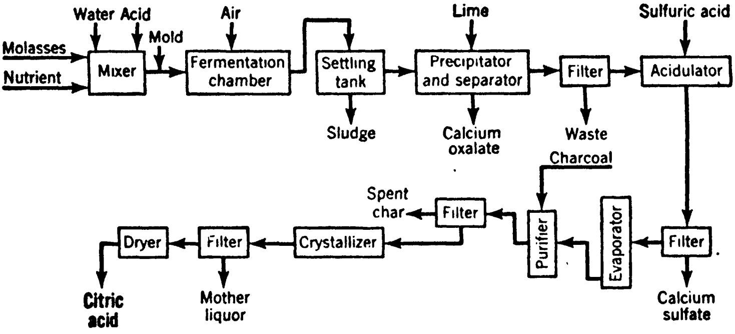
Location of Chromic-Acid Plants

CITRIC ACID



$$\begin{array}{c} CH_2COOH \\ | \\ HO{-}C{-}COOH \\ | \\ CH_2COOH \end{array}$$

From Molasses by Fermentation



Reaction

$$\underset{\text{Sucrose or dextrose}}{C_{12}H_{22}O_{11} \text{ or } C_6H_{12}O_6} + H_2O \xrightarrow[\text{Air}]{\text{Organism}} \underset{\text{Citric acid}}{C_6H_8O_7} + CO_2 + H_2O$$

35–65% weight yield

Material Requirements

Basis—1 ton citric acid

Molasses	8,000 lb	Sulfuric acid (95%)	1,400 lb
Nutrients	10–30 lb	Lime	1,000 lb

Process

Beet molasses (*ca.* 41°Bé) containing 48 to 52 per cent sugar by weight or cane molasses (*ca.* 40°Bé) of the blackstrap (52 to 57 per cent sugar) or high-test (70 to 80 per cent sugar) variety is introduced into a mixer. Dilute sulfuric acid is added to adjust the *p*H of the molasses between 5.5 and 6.5. Phosphorus, potassium, and nitrogen in the form of acids or salts are added as nutrients for proper mold growth in amounts depending on the nature of the raw material. The mix is then sterilized with live steam for about 0.5 hr and is finally diluted with water to a 15 to 20 per cent sugar concentration.

This ferment medium flows by gravity into shallow aluminum pans or trays, which are arranged in tiers in sterile fermentation chambers. The size and number of trays and chambers vary from plant to plant, but most chambers have provision for regulation and control of temperature, relative humidity, and air circulation. One plant has 80 trays per chamber with each tray holding about 100 gal of solution at a depth of 3 in.

The culture is prepared in a laboratory, using a special strain of *Aspergillus niger*. When the fermentation medium has cooled to about 30°C, it is inoculated with spores of this organism.

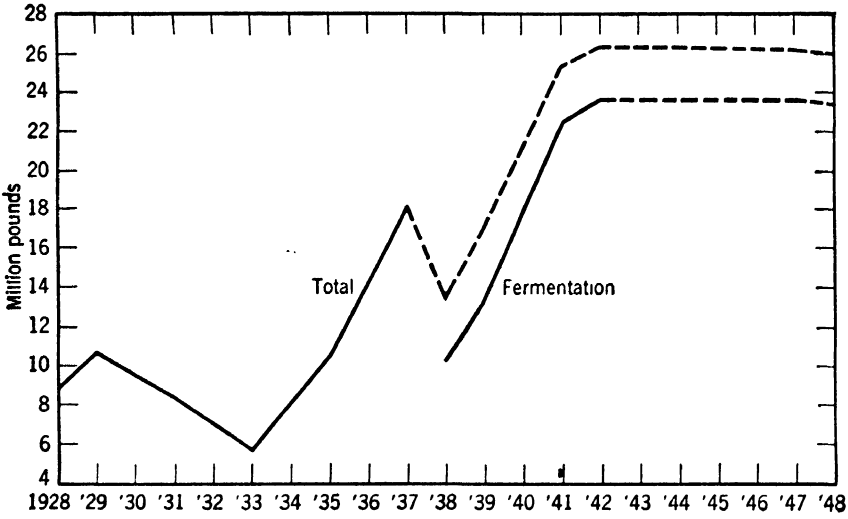
The fermentation requires 8 to 12 days, during which time evaporation reduces the volume of solution in each tray. The medium becomes more acid as the fermentation continues, and the course of the reaction may be followed by analyses; the *p*H of the solution drops to about 2 at the end of the fermentation, and the acid content varies from 10 to 20 per cent. The exact mechanism of the fermentation process is not well known, even though many hypotheses have been proposed. The temperature of the medium during fermentation is maintained at 28 to 32°C. Even with careful control of the temperature and the selection of high citric-acid-producing organisms, some oxalic and gluconic acids are formed. Purified air is generally circulated through the fermentation chamber, and the relative humidity is controlled between 40 and 60 per cent.

After the completion of each run, the fermentation chamber and trays are thoroughly sterilized, using water, dilute formaldehyde solution, and sulfur dioxide gas.

The crude fermented liquor is run into settling tanks and allowed to stand for several hours. The waste mold or mycelium mat is allowed to drain or is pressed to recover most of the fermented liquor and is then disposed of in any convenient manner. It may be used as fertilizer after proper weathering and processing. The clarified liquor from the settling tanks flows to precipitating tanks fitted with stirrers, where it is heated to a temperature of 80 to 90°C. The oxalic acid present is separated by preferential precipitation by the addition of a small amount of hydrated lime. The resulting calcium oxalate is worked up separately in a manner similar to the following process described for citric-acid recovery. Approximately 1 part of hydrated lime for every 2 parts of liquor is slowly added over a 1-hr period while the temperature is raised to about 95°C. The precipitated calcium citrate is filtered on a vacuum filter, and the filtrate is run to waste. The calcium citrate cake is run to acidulators, where it is acidified with dilute sulfuric acid. It is then filtered (the cake consists of calcium sulfate), and the citric-acid mother liquor is decolorized by a charcoal treatment. From the purifier the liquor goes to a vacuum evaporator where it is concentrated. It is then run into a crystallizer where, on cooling, citric acid crystallizes, generally in the form of the monohydrate. The resulting acid is of USP grade, and the over-all yield from the process varies from 35 to 65 per cent by weight, based on the sugar content of the raw material.

From Citrus Fruits

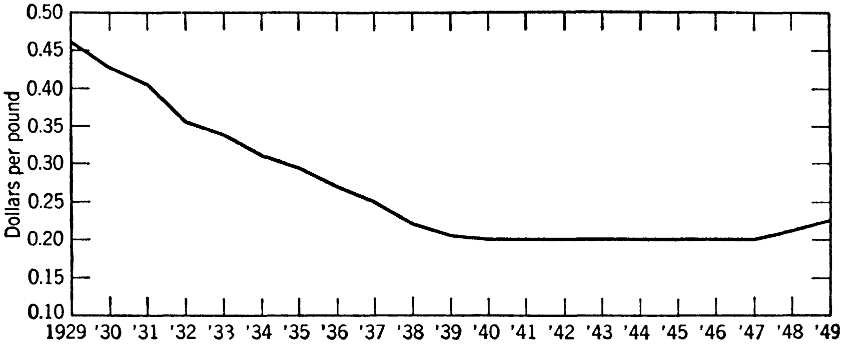
Citric acid occurs naturally in the juice of lemons, limes, pineapples, and other citrus fruits. The acid is extracted from the citrus juices by clarification, precipitation as calcium citrate, acidulation, concentration, and crystallization. The details of the extraction process depend on the nature of the raw material, but basically it is the same as that described for citric-acid recovery from the sugar-fermentation process. Seventy per cent recovery is usually attained.



Production—Citric Acid

Use Pattern

	Per cent
Food and soft drinks	40
Medicinals	30
Other	30
	100



Price—Citric Acid

Miscellaneous

Properties. Citric acid is generally produced containing one molecule of water (monohydrate) in the form of colorless, translucent crystals or white crystalline powder. It is odorless, has an acid taste, and is efflorescent in dry air. Anhydrous citric acid is also commercially available and may be produced by direct crystallization.

	Anhydrous ($C_6H_8O_7$)	Monohydrate ($C_6H_8O_7 \cdot H_2O$)
Mol. wt.	192.12	210.14
Sp. gr.	1.665 20°C/4	1.542
M.P.	153°C	Loses H_2O at 70–75°C
B.P.	Decomposes about 175°C	

Soluble in cold water (133 g per 100 g), cold (15°C) absolute alcohol (76 g per 100 g), and cold (15°C) ether (2.2 g per 100 g).

Grades. USP (crystals or powder) containing not less than 99.7 per cent citric acid monohydrate, C.P., and anhydrous.

Containers and Regulations. Barrels (230 lb), kegs, boxes, cartons, fiber drums, and bottles. No ICC shipping label required.

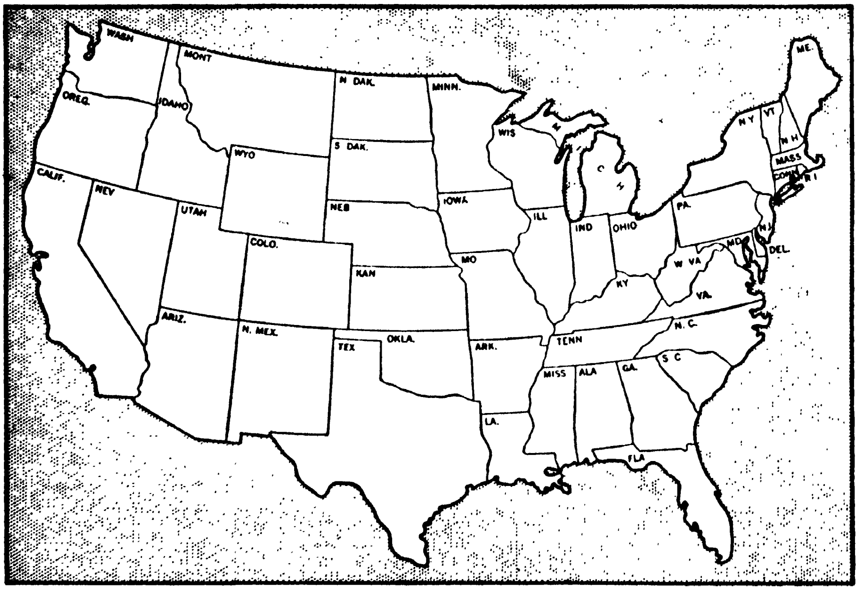
Economic Aspects

For years, citric acid was recovered from the juices of lemons, limes, and pineapples, which were expressed from cull fruit or obtained as a by-product of pineapple canning. In recent years (since 1919) the fermentation of dextrose or sucrose has been developed commercially and has superseded the older process because of economic factors. Some acid (less than 20 per cent) is still recovered from natural sources, but the older process cannot hope to fill current demands for citric acid in the food, soft-drink, and medicinal fields.

In common with most fermentations, the presently used process is difficult and requires an operating staff with a strong background in fermentation technology for economic and continued plant operation. Considerable work has been done on the development of a submerged culture process, and one such process utilizing *Aspergillus wentii*, in which no by-product oxalic and gluconic acids are formed, has at least been run on a pilot-plant scale.

Some competition in the food and beverage fields may be expected from lactic and malic acids, but to date industrial preference is overwhelmingly in favor of citric acid.

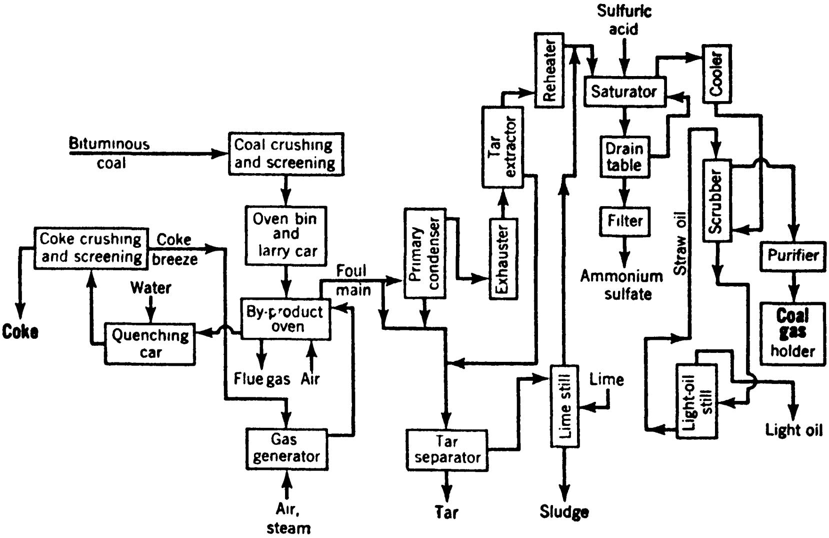
From a competitive standpoint, it is doubtful if a fermentation plant manufacturing less than 10,000,000 lb of acid annually would be economic. Citric-acid-recovery plants are usually a part of integrated juice-utilization plants, and so their size depends on other processing factors, such as the part-time use of equipment installed primarily for other purposes.



Location of Citric-Acid Plants

COKE AND COAL GAS

From By-Product Coking of Coal



Yield

70% coke based on coal charged

Material and Utility Requirements

Basis—1 ton coke plus 14,000 to 18,000 cu ft 550 Btu gas, 14.5 gal tar, 36 lb ammonium sulfate, and 3 to 6 gal light oil

Bituminous coal	2,860 lb	Water	1,500–3,000 gal
Sulfuric acid (60°Bé)	36 lb	Steam	570–860 lb
Lime	2–3 lb	Electricity	9–13 kw-hr

Process

Coke is produced by the high-temperature (900 to 1,000°C) distillation of coal by heating in the absence of air. This high-temperature carbonization (pyrolysis) also produces a variety of chemical compounds, which are collectively called "coke-oven" by-products or "coal chemicals." Among these products are coal gas (coke-oven gas), tar, light oil, and ammonia or ammonium sulfate.

The by-product coking oven is a narrow, tapered (for ease of discharge) chamber, which has a capacity of 12 to 16 tons of coal. Each oven is run intermittently, but, since a battery contains 30 to 90 ovens which are started and finished at different times, the over-all operation is continuous. There are several types of ovens, which differ from each other in detail rather than in principle. The major differences lie in the arrangement of the heating flues (vertical or horizontal), regenerative methods of preheating the combustion air, and arrangement of the heating gas and air inlets to the flues. Among the better-known and more widely used ovens are the Koppers-Becker (vertical flue) and Semet-Solvay (horizontal flue). The coal charge in these ovens is heated through both sidewalls so that heat travels toward the center of the charge. The heat is completely supplied by burning gases in the flues on the sides, so that no burning takes place in the oven. Producer or oven gas is burned to furnish the necessary heat.

Bituminous coal is crushed, screened, and loaded into an oven bin. It is transferred then by larry car to individual ovens (previously heated to 1,100°C) where it is dropped into charging holes. The first rush of air, steam, and gas is allowed to escape. After leveling the surface of the coal, the charging holes are covered, and heating is continued until the coal is completely coked. Volatile materials are evolved and pass to the recovery system. The average temperature at the center of the charge at the end of the heating period is about 1,000°C, whereas the flue temperature is about 1,225°C.

When the coking operation is completed, the doors on the ends of the oven are opened, and the entire incandescent mass is removed in less than 1 min by an electrically driven ram. The coke falls into a quenching car where it is quenched with water (wet quenching) or an inert gas (dry quenching) such as nitrogen or carbon dioxide. The latter method allows recovery of about 75 per cent of the sensible heat in the coke.

The cool coke is dumped onto a wharf from which it is conveyed to a crushing and screening plant. The breeze (fines) from this plant may be used to make producer gas by reaction with air and steam in a gas generator.

The volatile material (gas plus entrained liquid and solid particles) from the oven passes upward through a cast-iron gooseneck into a horizontal steel trough called the collecting, hydraulic, or foul main. A slight vacuum is maintained on this trough by a mechanical exhauster beyond the primary condenser. The condensed liquids (tar and ammonia-containing water) collecting along the bottom of the main are pumped to tar separators.

The uncondensed gases pass out of the foul main into a primary condenser and cooler. Here the temperature of the gas is reduced from 75 to 30°C. The condensed liquids and tars are discharged from the bottom of the condenser into a line carrying the liquids from the collecting main. The gases pass then to an exhauster, which compresses them, thus raising the temperature to approximately 50°C. About 75 per cent of the tar is removed because of the high-speed swirling motion imparted to the gases by the exhauster. After passing through a final tar extractor, the gases contain about 75 per cent of the ammonia and 95 per cent of the light oil present in the original coke-oven gas.

The tar from the extractor is discharged into a tar separator. Here a mixture of tar and ammonia water is separated by continuously decanting the aqueous ammonia. The decanted solution is run into a lime still where lime is added to liberate the fixed ammonia. This operation is necessary, since a large portion of the ammonia may be tied up as salts such as ammonium chloride. The free ammonia is distilled with steam and sent to the saturator. The crude tar is discharged from the bottom of the tar separator and is transferred to storage tanks. From here it is transported to open-hearth furnaces or boilers if it is to be used for fuel, or to tar-refining plants if it is to be distilled. The commercial products from the refinery consist of two types: crudes and chemicals. The principal crudes are wood-preserving oils, road tars, industrial pitches (for roofing and water-proofing), and pitch cokes. The wood-preserving oils are distillates; the other crudes are residues. For discussion of the chemicals produced by distilling coal tar, see *Naphthalene, Cresol, Benzene,* and *Phenol.*

The gases from the final tar extractor are passed through a reheater into a saturator containing dilute (5 to 10 per cent) sulfuric acid. At a temperature of about 60°C (maintained by the reheater and the heat of neutralization), the ammonia is absorbed, and crystalline ammonium sulfate is formed. The crystals are removed from the bottom of the saturator, allowed to drain on a table (the mother liquor is returned to the saturator), and dried in a centrifuge. For further details, see *Ammonium Sulfate.* Aqua ammonia may be obtained instead of the salt by passing the ammonia-containing gas into a water scrubber and concentrating the resulting solution by distillation. See *Ammonia* for details.

The warm gas (60°C) from the saturator is cooled to about 25°C in final condensers or coolers where it is scrubbed with water. Some naphthalene generally separates and is carried along to the bottom of the cooler, where it may be recovered from the waste water. The gas leaving the top of the cooler is sent to the bottom of a scrubber, in which it passes countercurrently to a stream of straw oil (a heavy petroleum fraction) or coal-tar oil. At about 25°C the oil absorbs approximately 2 to 3 times its weight of light oil and removes about 95 per cent of the light-oil vapor in the gas. The enriched straw oil flows from the bottom of the scrubbers through heat exchangers to a stripping column.

Here the straw oil flows downward into direct contact with live steam. Vapors of light oil and water pass through the afore-mentioned heat exchangers to condensers and water separators. The crude light oil is sent to fractionating columns for processing. See *Benzene*, *Toluene*, and *Xylene* for details. The stripped straw oil is re-used in the scrubbers. Good absorption of light oil requires from 10 to 15 gal of straw oil per 1,000 cu ft of gas.

The gas, leaving the top of the light-oil scrubber, is passed through either dry or wet purification units for sulfur (hydrogen sulfide and thiocyanate) removal. The more common processes include the iron oxide–wood shavings (dry), Seaboard, Ferrox, Thylox, Girbotol, and sodium phenate (wet) processes. The purified coke-oven gas is sent to gas holders, whence it is distributed for domestic consumption or is used as a heat source for the coke ovens. The average composition of the gas (by volume) is approximately 53 per cent hydrogen, 32 per cent methane, 6 per cent carbon monoxide, 4 per cent illuminants, 3 per cent nitrogen, 1.8 per cent carbon dioxide, and 0.2 per cent oxygen. The average colorific value per cubic foot ranges from 550 to 590 Btu.

A few by-product coke ovens are run at low temperatures (400 to 600°C). This low-temperature carbonization produces a greater amount of liquid products, and the coke obtained, called semicoke, contains from 8 to 20 per cent volatile material. The following table lists the approximate yields of coal carbonized by both methods as well as the variation in the resulting coal gas:

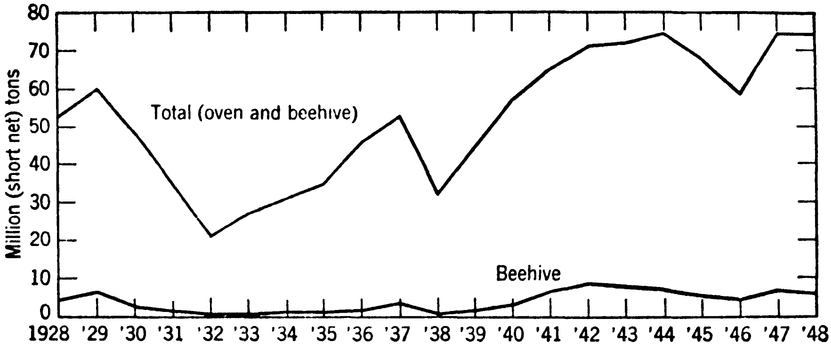
APPROXIMATE YIELDS PER TON OF COAL CARBONIZED

	High Temperature	Low Temperature
Furnace coke	1,300– 1,550 lb	
Coke breeze	70– 100 lb	
Semicoke (12 per cent volatiles)		1,500 lb
Tar	8– 12 gal	30 gal
Ammonium sulfate	17– 25 lb	10 lb
Light oil (from gas scrubbers)	2– 4 gal	2 gal
Gas (550 Btu)	10,000–12,000 cu ft	
Gas (950 Btu)		3,000 cu ft

VARIATION IN THE PURIFIED GAS OBTAINED

	1,000°C, per cent	500°C, per cent
Hydrogen	50	10
Methane and homologs	34	65
Carbon monoxide	8	5.5
Illuminants	3.5	8
Carbon dioxide	2.5	9
Nitrogen	2	2.5

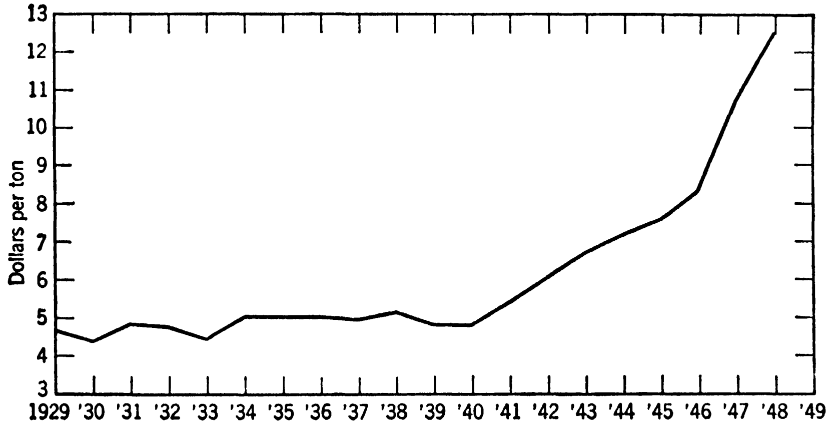
Another method of producing coke is known as beehive coking. This older process produces a hard, strong, cellular (beehive) coke, which is preferred by some metallurgical consumers. Since by-products are wasted, this process does not compare favorably with the newer by-product methods and accounts for only a relatively small percentage of total coke production at the present time.



Production—Coke

Use Pattern

Coke	1948 (est.), per cent
Blast furnaces (metallurgical)	80
Producer gas and water gas	6
Domestic uses	5
Iron foundries	5
Other industrial	4
	100



Price—Coke (Average value at plant)

Economic Aspects

Coke is usually the main product of coal carbonization processes, and gas one of the by-products, although in certain cases retorts are operated to produce gas as the chief product. Coke, however, is by far the more important of the two. In the early days of the industry, it was produced in beehive ovens, and the gas was often wasted. The need for by-products, more and better coke, and clean gas led to the adoption of by-product ovens. In early 1939, there were less than a thousand beehive ovens in operating condition, but war requirements led to the rehabilitation of older beehive ovens until a peak of nearly 14,000 (only 20 per cent less numerically than the by-product ovens in use) was reached in 1943. Most of these have since been abandoned. The average capacity of a beehive oven is quite small compared to that of the by-product oven, and so even in 1943 less than 12 per cent of the total coke production came from beehive ovens. The yield of coke in a by-product oven is better than 70 per cent based on the coal charged, whereas beehive yields are less than 65 per cent.

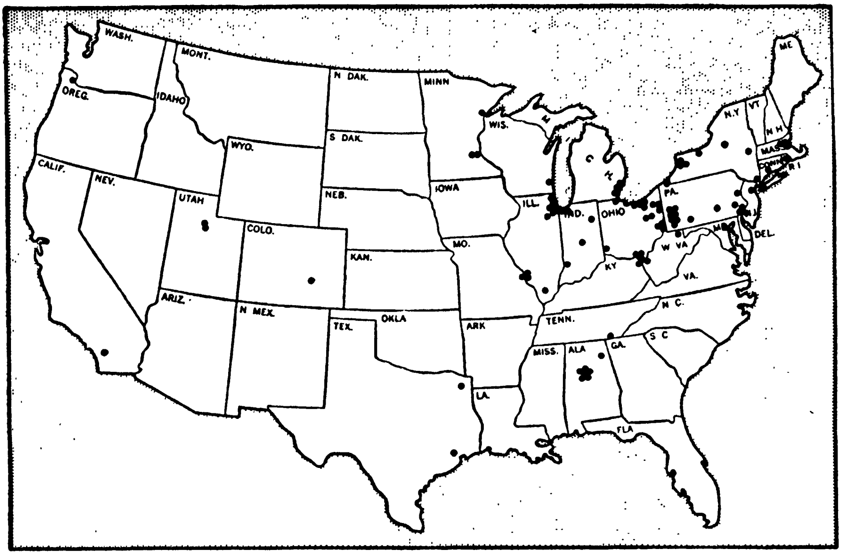
Most coke-oven installations (usually 70 to 80 per cent of production) are so-called "furnace plants" owned and operated by blast-furnace operators. "Merchant plants" generally make coke for domestic and nonmetallurgical uses. Small amounts of coke (less than 2 per cent) are made in low-temperature coking installations and in gas plants (gas-house coke). These products normally go to domestic-fuel markets. Two to three per cent of total coke production is petroleum coke, a preferred raw material for electrode manufacture. A substantial quantity is also used as domestic fuel in certain sections.

Of the gas produced in by-product ovens (17 per cent of coal charged), 37 per cent is used to heat the ovens. The remainder is sold usually to neighboring metallurgical and industrial plants and public utilities. In many sections of the United States, coke-oven gas for domestic (and some industrial) use has been largely replaced by natural gas. With the conversion of the "Big Inch" and "Little Inch" pipelines to this service, this trend should continue unless threatened legislation for Government control of natural-gas utilization materializes.

Large-scale experiments are now underway for the controlled underground gasification of impure coal and seams too thin to mine. Successful culmination of these experiments may lead to wide distribution of coal gas and more nearly complete recovery of coal.

The future of the by-product coke industry is intimately tied up with the steel industry. The activity of the latter affects the former directly. If iron and steel are ever replaced to a large extent by plastics and light metals, coke production may be expected to drop. A slight increase in the use of coke for domestic fuel may be expected in the future, as city antismoke ordinances are passed and enforced.

The size and investment cost of by-product coke plants is discussed under other chapters (see *Ammonium Sulfate*, *Benzene*, and *Cresol*).



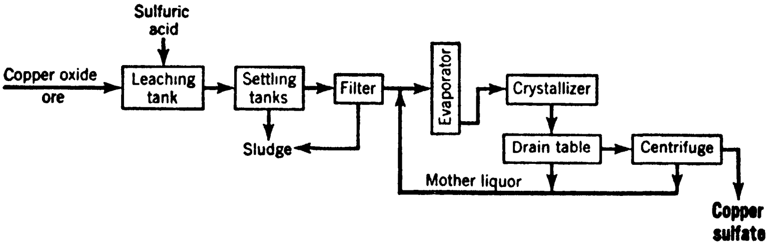
Location of By-Product Coke Oven Plants

COPPER SULFATE

(CUPRIC SULFATE)

$CuSO_4 \cdot 5H_2O$

From Cupric Oxide and Sulfuric Acid



Reaction

$$CuO + H_2SO_4 + 4H_2O \rightarrow CuSO_4 \cdot 5H_2O$$

99% yield

Material Requirements (Theoretical)

Basis—1 ton cupric sulfate pentahydrate

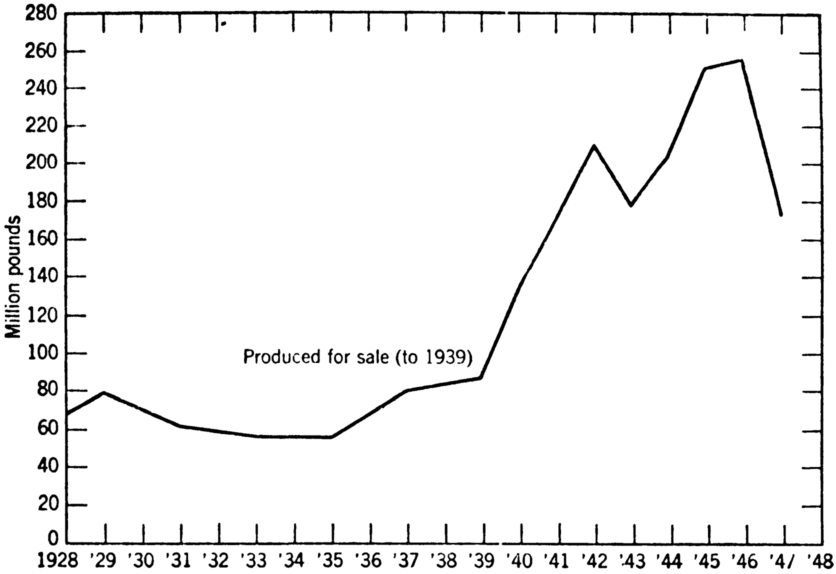
Copper oxide	640 lb
Sulfuric acid (100%)	785 lb

Process

Cupric (copper) sulfate is produced by the action of sulfuric acid on copper oxide ores such as azurite and malachite. The ore is leached with sulfuric acid by percolation (about 8 days) through the ore in large rectangular tanks. Alternately, heavy agitators may be substituted for the tanks if necessary. The resulting copper sulfate solution is allowed to settle and may be filtered to obtain a clear solution.

The solution is sent to evaporators and then to crystallizers to form crystalline cupric sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$). The crystals are allowed to drain and may be dried by centrifuging.

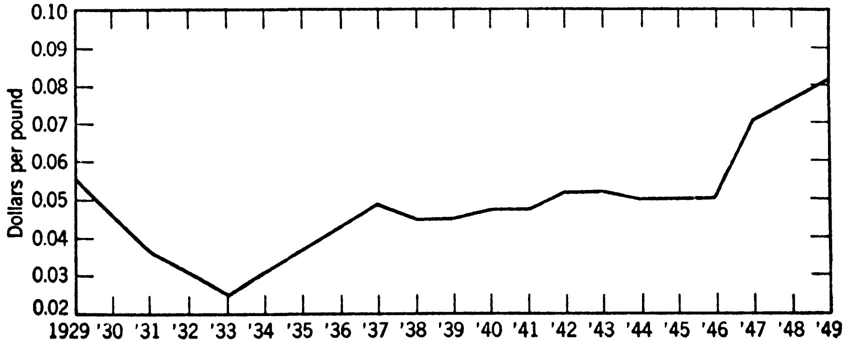
A large percentage of the cupric sulfate on the market is obtained as a by-product in copper refining. Copper is often leached from its ores with sulfuric acid. The resulting solution is treated in an electrolytic cell using an insoluble anode. Copper is plated at the cathode regenerating sulfuric acid. The acidic copper sulfate solution leaving the cell may then be re-used on a fresh batch of ore. The cell solution after re-use may be pumped to lead-lined tanks for evaporation and crystallization of copper sulfate pentahydrate.



Production—Copper Sulfate

Use Pattern

	Per cent
Agriculture	50
Mining and metal industries	15
Miscellaneous	35
	100



Price—Copper Sulfate

Miscellaneous

Properties. $CuSO_4 \cdot 5H_2O$. Crystallizes from water as the pentahydrate in the form of blue triclinic crystals which slowly effloresce in air.

Mol. wt.	249.71	M.P.	Loses $4H_2O$ at 110°C
Sp. gr.	2.286 15.6°C/4	B.P.	Loses $5H_2O$ at 250°C

Soluble in water (24.3 g per 100 g at 0°C, 205 g per 100 g at 100°C).

The anhydrous salt ($CuSO_4$) is obtained by dehydration as greenish-white rhombic crystals.

Mol. wt.	159.63	M.P.	200°C
Sp. gr.	3.606 (15°C)	B.P.	Forms CuO at 650°C

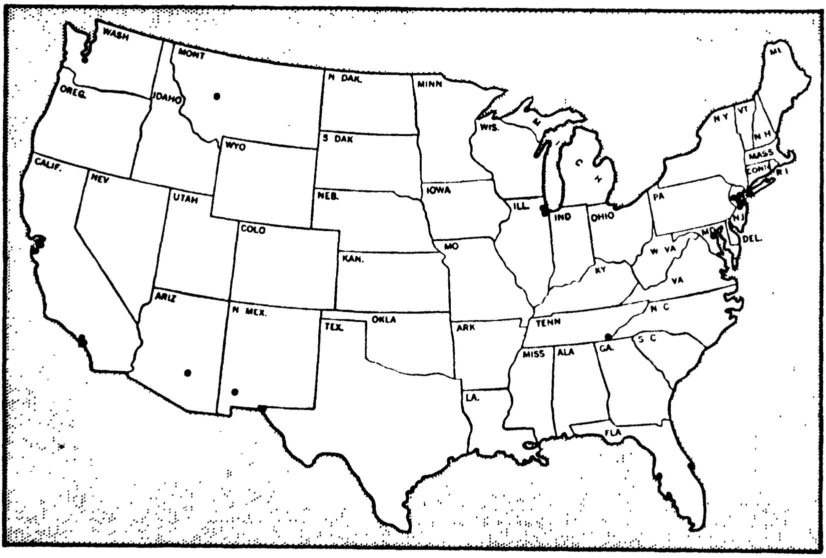
Soluble in water (14.3 g per 100 g at 0°C, 75.4 g per 100 g at 100°C). Insoluble in alcohol.

Grades. The common commercial form is the pentahydrate ($CuSO_4 \cdot 5H_2O$) in technical (99 per cent), USP, and C.P. grades.

Containers and Regulations. Barrels, kegs, bags, boxes, and bottles. Material is considered poisonous. No ICC shipping label required.

Economic Aspects

Approximately 20 to 30 per cent of the copper sulfate on the market is a by-product of primary copper refining, made by simple crystallization of refinery liquors. The remainder is made by treating scrap cop-



Location of Copper Sulfate Plants

per with dilute sulfuric acid in the presence of air to produce liquors from which copper sulfate may be crystallized. Much larger quantities could be recovered than are salable, but uses appear to be stable, and demand does not fluctuate much. Production increased during the war years, chiefly because of export demands and increased use in agriculture.

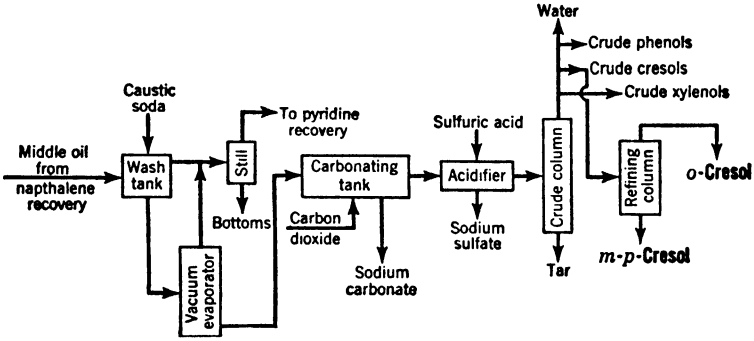
Copper refineries are usually quite large and keep their crystalline copper sulfate operation at as low a volume as possible. Plants operating on scrap copper can be of almost any size and frequently operate with cheap reconditioned equipment.

CRESOL

(CRESYLIC ACID)

$CH_3C_6H_4OH$

From Coal Tar



Yield

0.3 to 1.1% crude cresol from coal tar
(0.1 gal per ton of coal)

Material Requirements (Theoretical)

Basis—1 ton of refined cresols

Middle oil	Variable	Sulfuric acid (100%)	1,850 lb
Caustic soda (50%)	1,500 lb	Carbon dioxide	May replace part of sulfuric acid

Process

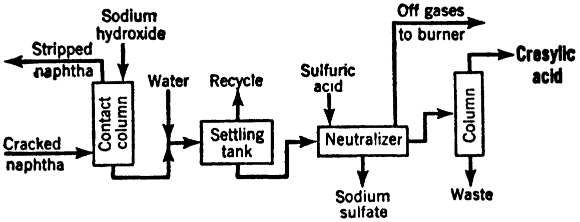
Cresol (cresylic acid) is an isomeric mixture (*o*-, *m*-, and *p*-cresol) obtained by refining the so-called tar acids. These acids comprise the phenolic constituents present in coal tar. The by-product coking of coal (see *Coke*) yields an average of 10 gal of coal tar per ton of coal. The tar is distilled (see *Naphthalene*), and a fraction known as middle oil, creosote oil, or tar-acid oil is collected. This fraction, constituting 10 to 20 per cent of the tar (average about 17 per cent), is first processed to remove most of the naphthalene. The phenols and cresols, present in the tar to the extent of 0.3 to 1.1 per cent, are then removed as follows:

The tar-acid oils, after naphthalene removal, are charged into a wash tank where the phenolic bodies are extracted with sodium hydroxide solution. Caustic concentrations varying from 8 to 50 per cent may be utilized, although the higher concentrations are in more general use. The tar acids are converted into their respective salts, sodium phenate and cresylate, which are soluble in the aqueous layer. This layer containing the tar-acid salts is allowed to settle in the wash tank and is then discharged from the bottom. The nonaqueous (neutral-oil) layer is distilled and sent to the pyridine-recovery plant (see *Pyridine*).

The sodium cresylate from the wash tank is freed of entrained and dissolved oils and bases by evaporation (under vacuum) to controlled concentrations. The concentrated cresylate solution is run from the evaporator into a neutralizer or carbonating tank. Here most of the salts are converted into free tar acids by treatment with carbon dioxide. The acids are decanted from the resulting sodium carbonate solution and are then charged into an acidifier. Sulfuric acid, in varying concentrations, is added to complete the process of "springing" the tar acids. Some plants use sulfuric acid entirely, thus eliminating the carbon dioxide treatment, but this is not the usual practice. The released phenols and cresols (tar acids) are separated from the aqueous sodium sulfate solution in the acidifier by decantation. The top layer, containing the phenolic bodies, is distilled either intermittently or continuously through a fractionating column. Here the water is removed, and several fractions such as crude phenols, cresols, and xylenols are taken. The phenol fraction is sent to the phenol-refining plant for further processing (see *Phenol*).

The crude cresol cut is further purified by fractional distillation to yield *o*-cresol and a mixture consisting of *m*- and *p*-cresol. The latter cresols are generally marketed as a mixture since their separation is considerably more difficult than the isolation of *o*-cresol. The two isomers (meta–para) may be refined by the formation of the oxalic-acid addition product or by alkylation with an olefin (isobutylene) to yield compounds that are more readily separated. Hydrolysis and dealkylation, respectively, yield refined *m*- and *p*-cresols. However, only a small fraction of the *m*–*p*-cresol mixture is used to prepare the individual isomers.

From Petroleum (Cracked Naphtha)



Material Requirements

Basis—1 ton cresylic acid

Cracked naphtha	Variable
Sodium hydroxide *	740 lb
Sulfuric acid *	1,820 lb

Process

In the thermal cracking of petroleum, there are formed certain cresylic bodies known as petroleum acids. Sometimes these acids occur in sufficient concentration in the cracked naphthas and gas-oil fractions to warrant recovery. The petroleum acid-recovery methods are very similar to the cresol-recovery processes used by the coal-tar distillers.

Cracked naphtha is passed through a vertical, packed contact column countercurrent to a solution of sodium hydroxide (caustic soda). A solution of sodium cresylate forms, which is drawn off the bottom of the contactor. After being diluted with water, the solution is run to a settling tank, where it is allowed to stand until two layers separate. The hydrocarbon oil layer is drawn off the top of the settling tank and recycled.

The diluted sodium cresylate solution is discharged from the bottom of the tank and charged batchwise into a gastight, air-agitated reactor. Here the solution is neutralized to a controlled *p*H by the addition of sulfuric acid. The gases formed are piped to a furnace where they are burned before being discharged to the atmosphere. The sodium sulfate solution, which is obtained in the neutralization step, separates and is discharged from the bottom of the reactor to waste.

Crude cresylic acid is drawn off the top of the reactor and run to a batch distillation column. The column operates under increasing vacuum as the distillation progresses in order to maintain low distillation temperatures. Various cuts of cresylic acid are taken, ranging from 350 to 525°F. The ortho isomer and meta-para isomer mixture are obtained. These grades are adjusted by proper blending to meet a variety of customers' specifications.

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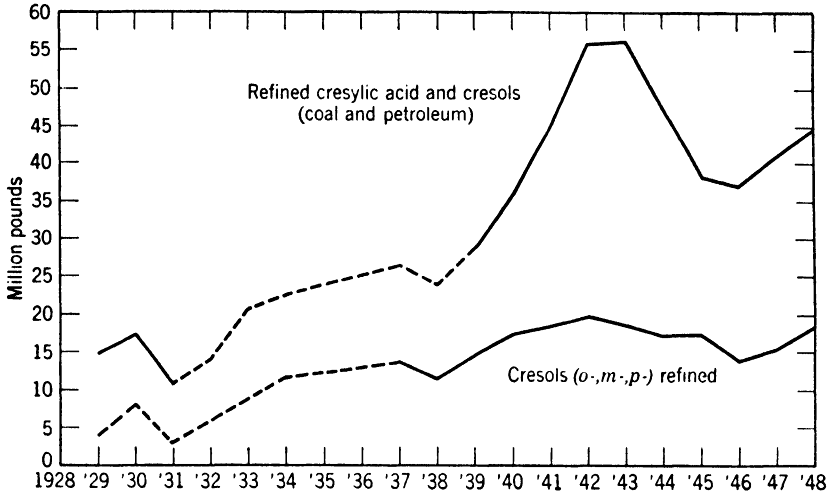
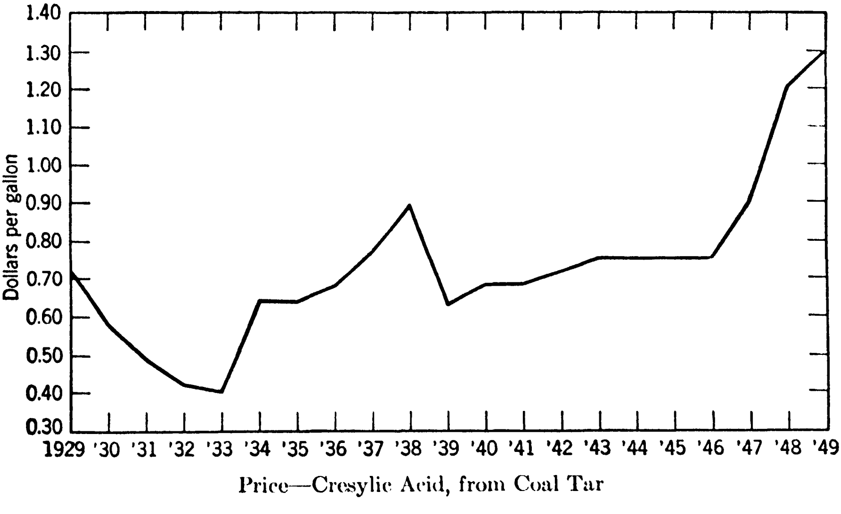
* Theoretical amounts based on cresol content of feed.



Production—Cresols and Cresylic Acid

Use Pattern

	Per cent
Plastics and plasticizers	60
Ore-flotation chemicals	10
Disinfectants and insecticides	10
Textiles, medicinals, dyes, and inks	10
Other, including petroleum	10
	100



Price—Cresylic Acid, from Coal Tar

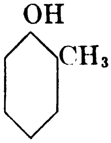
Miscellaneous

Properties. *Cresylic Acid* (mixture of *o*-, *m*-, and *p*-cresols). Yellowish liquid with a phenol-like odor.

Soluble in alcohol, ether, and chloroform. Slightly soluble in water.

Grades. Cresol, USP (isomeric mixture having sp. gr. 1.030 to 1.038 at 25°C, 90 per cent by volume distils between 195 to 205°C). Metaparacresol is a mixture of about 40 per cent meta and 60 per cent para. Cresylic acid is sold in a wide variety of technical and special grades depending on color and distillation range.

Containers and Regulations. Tank cars, drums, barrels, carboys, cans, and bottles. No ICC shipping label required.

Properties. *o-Cresol,*  . White crystals with a phenol-like odor.

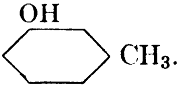
Mol. wt.	108.13	M.P.	30.8°C
Sp. gr.	1.048 20°C/4	B.P.	190.8°C

Soluble in alcohol, ether, and chloroform. Slightly soluble in water (2.5 g per 100 g at room temperature).

Flash point (closed cup)	178°F
Vapor density (air = 1)	3.72

Grades. Technical.

Containers and Regulations. Drums, barrels, carboys, cans, and bottles. No ICC shipping label required.

Properties. *m-Cresol,*  Colorless to yellowish liquid with a phenol-like odor.

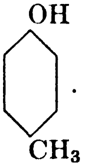
Mol. wt.	108.13	M.P.	10.9°C
Sp. gr.	1.034 20°C/4	B.P.	202.8°C

Soluble in alcohol, ether, and chloroform. Slightly soluble in water.

Flash point (closed cup)	187°F
Vapor density (air = 1)	3.72

Grades. Same as *o*-cresol.

Containers and Regulations. Same as *o*-cresol.

Properties. *p-Cresol,*  . Crystalline mass with a phenol-like odor.

Mol. wt.	108.13	M.P.	36°C
Sp. gr.	1.035 20°C/4	B.P.	202°C

Soluble in alcohol, ether, and chloroform. Slightly soluble in water.

Flash point (closed cup)	187°F
Vapor density (air = 1)	3.72

Grades. Same as *o*-cresol.

Containers and Regulations. Same as *o*-cresol.

Economic Aspects

Cresol is chiefly a product of the coal-tar distillation industry, with small amounts recovered directly by the by-product coke industry. Most cresol is sold in the crude state as creosote oil or partially refined as mixed cresylic acid. In 1947 tar distillers accounted for a little more than 122,000,000 gal of creosote-oil production; coke-oven operations produced about 39,000,000 gal. The creosote-oil fraction usually amounts to 10 to 20 per cent by volume of the tar.

The creosote oil is often used as such as a wood preservative or for "oiling back" pitch to make it suitable for road tar and roofing tar. At other times, the naphthalene is removed and refined, and the remaining "tar acids" are used as such. These tar acids may be separated into phenol and a distilled grade of cresylic acid (95 to 100 per cent cresols) suitable for resin manufacture. Besides the various cresol isomers, cresylic acid usually contains xylenols, the presence of which is preferred in certain cases, as in the manufacture of the plasticizer tricresyl phosphate. Separation into the various isomers is difficult and expensive and is practiced only to a small extent.

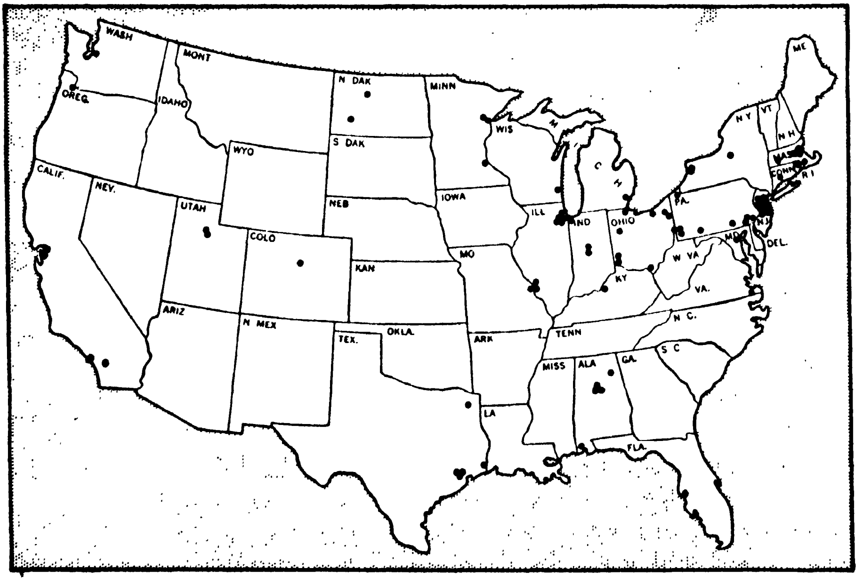
Demand for tar acids was sufficient during World War II that several by-product coke-oven operators added tar acid–naphthalene facilities to their existing plants, the light oils being handled in the existing by-product plant. A general cost figure for such plants would be difficult to estimate, because of the great variation in operating characteristics among various plants. Plants with distilling capacities between 5,000,000 and 10,000,000 gal per yr may cost between $30 and $100 per 1,000 gal annual distilling capacity, depending on the products recovered. Redistillation of tar-acid oils yields an acid-soluble cut from which pyridine and other nitrogen bases may be recovered (see *Pyridine*).

Minor competition for creosote oil as a wood preservative is afforded by wood creosote, a product of the wood-distillation industry. During World War II, a shortage of creosote oil in Germany led to the use of a synthetic wood preservative consisting of 84 per cent sodium fluoride, 8 per cent xylenol, and 8 per cent caustic soda. Although expensive, the product was said to be highly effective.

Cresols may also be produced synthetically from toluene by processes similar to those by which synthetic phenol is produced from benzene (see *Phenol*). An example would be the hydrolysis of chlorotoluene to produce a mixture of *m*- and *p*-cresols along with a small amount of the ortho isomer. Large-scale demand for pure cresols could bring such a process into existence. Cost of such a plant would probably be slightly greater than that of a phenol plant of the same capacity. Sulfonation of toluene followed by alkali fusion is also possible (see *Phenol*), but it is doubtful if this process could compete with the hydrolysis of chlorotoluene.

A new plant currently under construction will make use of a newly developed process in which toluene vapors are bubbled through a liquid made up of sulfuric acid and a boron compound. A complex compound of the toluene and the boron chemical is formed, which, on hydrolysis, yields a cresol mixture. The economic potentialities of the process are interesting.

On the other hand, if coal hydrogenation plants are ever built in the United States, cresol supplies could be greatly augmented. A plant processing 10,000 tons of coal per day would yield nearly 200 tons per day of a by-product phenol–cresol–xylenol mixture.

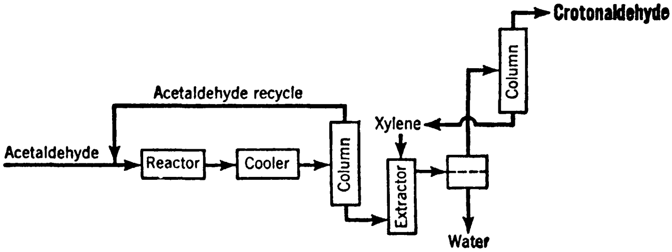


Location of Cresylic-Acid, Creosote-Oil, and Crude Tar-Acid Plants

CROTONALDEHYDE

$CH_3CH{=}CHCHO$

From Acetaldehyde via Aldol



Reaction

$$CH_3CHO + CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO$$

$$CH_3CH(OH)CH_2CHO \rightarrow CH_3CH{=}CHCHO + H_2O$$

75–80% yield

Material Requirements

Basis—1 ton crotonaldehyde

Acetaldehyde	3,250 lb
Xylene	Losses only

Process

Crotonaldehyde is produced by the dehydration of the aldol condensation product of acetaldehyde. The reaction may be carried out in a two-stage process. Acetaldehyde, in the presence of small amounts of dilute alkali, undergoes an aldol condensation to yield acetaldol (β-hydroxy butyraldehyde). When this product is heated in the presence of dilute mineral acids, dehydration takes place, resulting in the formation of crotonaldehyde. The latter may also be produced by a single operation in a continuous manner without the use of a catalyst. This process is more applicable to large-scale operations and does not require the careful controls needed in the two-stage method.

A 25 per cent aqueous solution of acetaldehyde (preferably freshly distilled) is pumped through a heated coil reactor (copper or stainless steel) under a pressure of 450 psi. The temperature of the reactor is maintained at about 160°C by a liquid bath. A contact time of about 2 hr is obtained by adjusting the flow rate.

The hot liquid products are passed through a condenser, where they are cooled while still under pressure. The cooled reaction products are run into a column, where the pressure is released and the unreacted acetaldehyde is distilled off. The acetaldehyde is recycled to the reactor.

The residual aqueous solution of crotonaldehyde is run into countercurrent extractors, where the aldehyde is extracted with xylene. The water and xylene layers are separated by decantation, and the latter is run to a column. The water layer, containing small amounts of aldol, may be recycled in conjunction with the acetaldehyde. The xylene fraction is distilled to yield crotonaldehyde; the residual xylene may be re-used in the extractors.

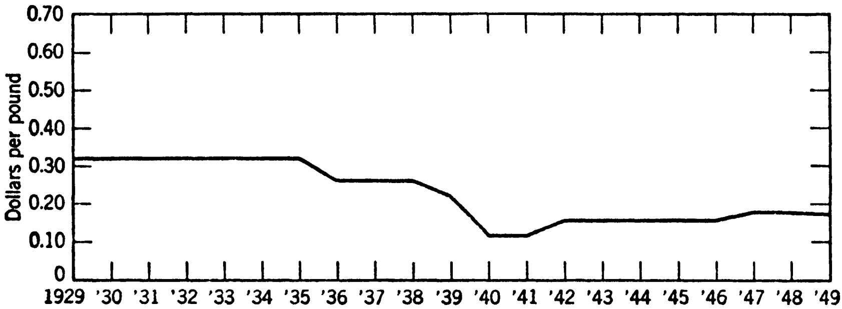
About 56 per cent of the acetaldehyde is consumed in one pass through the reactor. Unreacted aldehyde is recovered and recycled. Of the acetaldehyde consumed per pass, about 85 per cent is recovered as crotonaldehyde, making the over-all yield 75 to 80 per cent.

Production

No data available.

Use Pattern

Chemical manufacture Solvent	No breakdown available



Price—Crotonaldehyde

Miscellaneous

Properties. Colorless, flammable, lachrymatory liquid with a pungent suffocating odor; turns yellow on contact with air and light.

Mol. wt.	70.09	M.P.	−69°C
Sp. gr.	0.853 20°C/20	B.P.	102.4°C

Soluble in water (18 g per 100 g at room temperature) and miscible in all proportions with alcohol, ether, benzene, toluene, gasoline, and solvent naphtha.

Flash point (closed cup)	55°F
Vapor density (air = 1)	2.41
Explosive limits (% by volume in air)	Lower 2.95
	Upper 15.5

Grades. Technical (99 per cent).

Containers and Regulations. Drums and bottles. Red ICC shipping label required.

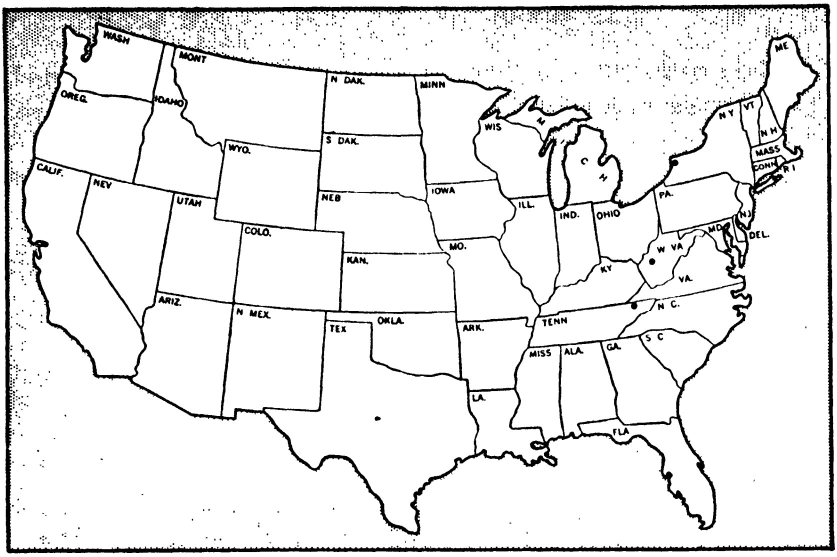
Economic Aspects

Crotonaldehyde is not a particularly important organic chemical at present from a general market standpoint, but the process by which it is manufactured offers great possibilities for a variety of organic-chemical manufactures. Since crotonaldehyde is derived from acetaldehyde, the process offers a method of increasing molecular size from two carbons to four. A substantial quantity of crotonaldehyde (about 70,000,000 lb per yr) is currently manufactured and used by its producers in the manufacture of synthetic butanol (see *Butyl Alcohol*).

By vapor-phase oxidation crotonaldehyde can be readily converted to maleic anhydride and has distinct possibilities in that direction. Being an aldehyde, it may also be used in the manufacture of phenol–aldehyde resins. One of these resins is said to have leather-tanning properties. The simple oxidation product of crotonaldehyde, crotonic acid, shows considerable promise in the resin and coating fields. In some cases, the precursor of crotonaldehyde, acetaldol, may also be used as an intermediate chemical, as in the hydrogenation of aldol to 1,3-butylene glycol.

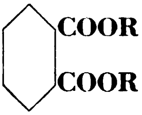
The future importance of crotonaldehyde may actually be secondary to that of acetaldol, since the latter compound may be further condensed with acetaldehyde to yield, by various secondary decarboxylation, dehydration, and other chemical reactions, a wide variety of organic compounds, including those with an aromatic nucleus.

Data on current production and size of crotonaldehyde plants in the United States are not available because of the small number of producers. However, the large German plant at Hochst had a capacity of 2,000 tons of crotonaldehyde per month.



Location of Crotonaldehyde Plants

DIALKYL PHTHALATES



Dimethyl: R = $-CH_3$

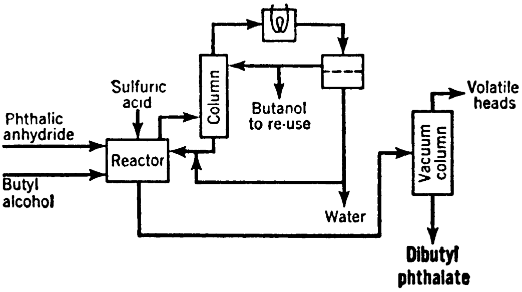
Diethyl: R = $-CH_2CH_3$

Dibutyl: R = $-(CH_2)_3CH_3$

Diamyl: R = $-(CH_2)_4CH_3$

From Phthalic Anhydride and Alcohol by Esterification

Example: Dibutyl phthalate



Reaction

$$C_6H_4(CO)_2O + 2C_4H_9OH \xrightarrow{H_2SO_4} C_6H_4(COOC_4H_9)_2 + H_2O$$

90% yield

Material Requirements

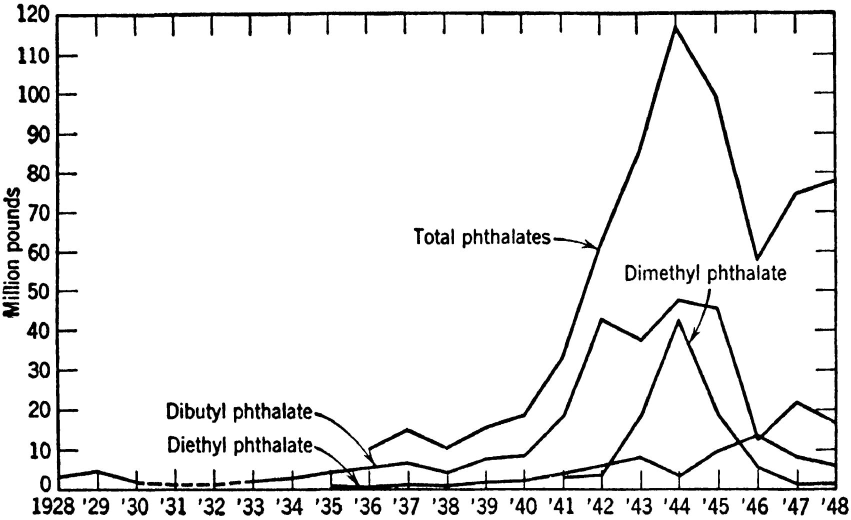
Basis—1 ton butyl phthalate

Phthalic anhydride	1,200 lb
Butyl alcohol (normal)	1,350 lb
Sulfuric acid (66°Bé)	10–25 lb

Process

The dialkyl phthalates are produced by esterifying phthalic anhydride with the appropriate alcohols in the presence of catalytic amounts of sulfuric acid. The process is essentially the same for all the lower aliphatic alcohols, and modifications are necessary only in the alcohol-recovery and product-purification systems.

Dibutyl phthalate is manufactured by charging approximately equivalent amounts of phthalic anhydride and normal butyl alcohol into a reactor. About 1 per cent of concentrated sulfuric acid (66°Bé) is added as catalyst. The reactor is equipped with an efficient agitator and internal steam coils for heating. The reactor is heated to such a temperature (150 to 200°C) that the binary azeotrope of water (38 per cent) and butanol (62 per cent) distils at a column-head temperature of approximately 93°C. The distillate is cooled and separated by decantation. The butyl alcohol layer is returned to the column, and the water layer is run either to recovery or to waste. When the optimum amount of water has been removed from the reactor, the residual crude butyl phthalate is discharged and run to a vacuum column. Any volatile impurities present are removed as vapors, which are condensed. The butyl phthalate is either stored or if necessary further purified by decolorizing with activated charcoal. The yield of dibutyl phthalate (99 per cent) based on the phthalic anhydride charged is about 90 per cent.



Production—Dialkyl Phthalates

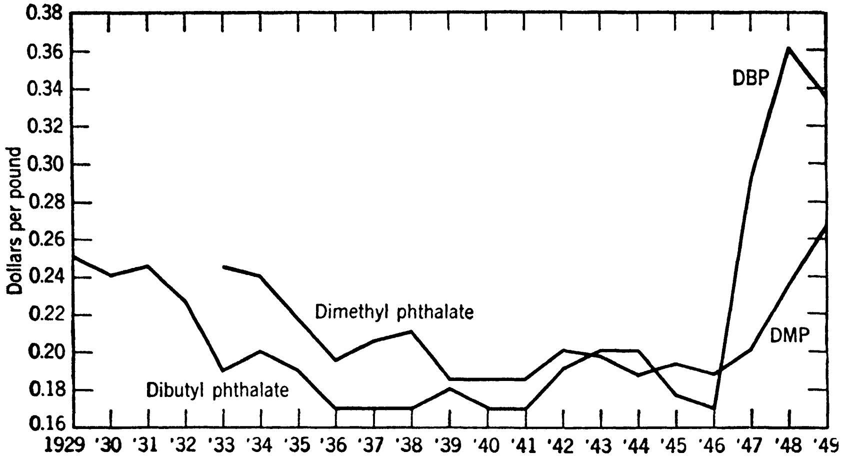
Dimethyl and *diethyl phthalates* are generally manufactured in batch esterification units similar to the one shown on the flowsheet for dibutyl phthalate production. However, benzene is usually introduced into the column to reduce the partial pressure of the alcohol. In the presence of benzene there is a tendency to drive the alcohol back down the column, while the water is removed in the form of a ternary azeotrope. The ternary mixture of alcohol, water, and benzene is condensed and separated by decantation. The benzene is returned to the column, while the water and alcohol are rectified to recover the alcohol for re-use.

The distillation is allowed to run until only crude phthalic ester remains in the still (reactor). The crude product is purified by vacuum distillation.

Diamyl and *dioctyl phthalates* are produced in a manner similar to dibutyl phthalate. The alcohol-recovery problem is much simpler in these three esters than in the manufacture of the methyl and ethyl esters, and so the recovery system may be eliminated. The water layer is either discarded or worked up in general-purpose distillation equipment, depending on the economics of the particular plant.

Use Pattern

	Per cent
Diamyl phthalate	
Plasticizer	100
Dibutyl phthalate	
Plasticizer	95
Miscellaneous, including insect repellent	5
	100
Diethyl phthalate	
Plasticizer	99
Miscellaneous	1
	100
Dimethyl phthalate	
Insect repellent	50
Plasticizer	50
	100
Dioctyl phthalate	
Plasticizer	100



Price—Dialkyl Phthalates

Miscellaneous

Properties. *Dimethyl Phthalate* [$C_6H_4(COOCH_3)_2$]. Colorless, odorless oily liquid, which is lightfast and apparently nontoxic.

Mol. wt.	194.18		
Sp. gr.	1.189 25°C/25	B.P.	282.0°C

Weight per gallon 9.93 lb (20°C)

Soluble in common organic solvents. Very slightly soluble in water (0.43 per cent).

Flash point (closed cup)	270°F
Vapor density (air = 1)	6.69

Properties. *Diethyl Phthalate* [$C_6H_4(COOC_2H_5)_2$]. Colorless, odorless, nonflammable oily liquid having a bitter taste.

Mol. wt.	222.23	M.P.	−40.5°C
Sp. gr.	1.121 25°C/25	B.P.	298-299°C

Weight per gallon 9.31 lb (20°C)

Soluble in alcohol and ether. Insoluble in water.

Flash point (closed cup)	325°F
Vapor density (air = 1)	7.66

Properties. *Dibutyl Phthalate* [$C_6H_4(COOC_4H_9)_2$]. Colorless, nonvolatile, stable oily liquid which is apparently nontoxic.

Mol. wt.	278.34	M.P.	−35°C
Sp. gr.	1.045 (21°C)	B.P.	340°C

Weight per gallon 8.72 lb (20°C)

Soluble in alcohol, benzene, ether and acetone. Very slightly soluble in water (0.04 per cent at 25°C).

Flash point (closed cup)	315°F
Vapor density (air = 1)	9.58

Properties. *Diamyl Phthalate* [$C_6H_4(COOC_5H_{11})_2$]. Colorless, practically odorless, stable, nonflammable liquid which is apparently nontoxic.

Mol. wt.	306.39		
Sp. gr.	1.023 (20°C)	B.P.	247–255 (50 mm)°C
	Weight per gallon	8.52 lb (20°C)	

Soluble in most lacquer solvents and diluents, oils, and hydrocarbons. Insoluble in water.

Flash point (closed cup) 357°F

Grades. Technical (98 to 99 per cent).

Containers and Regulations. Tank cars, drum cars, steel drums, carboys, cans, and bottles. No ICC shipping label required.

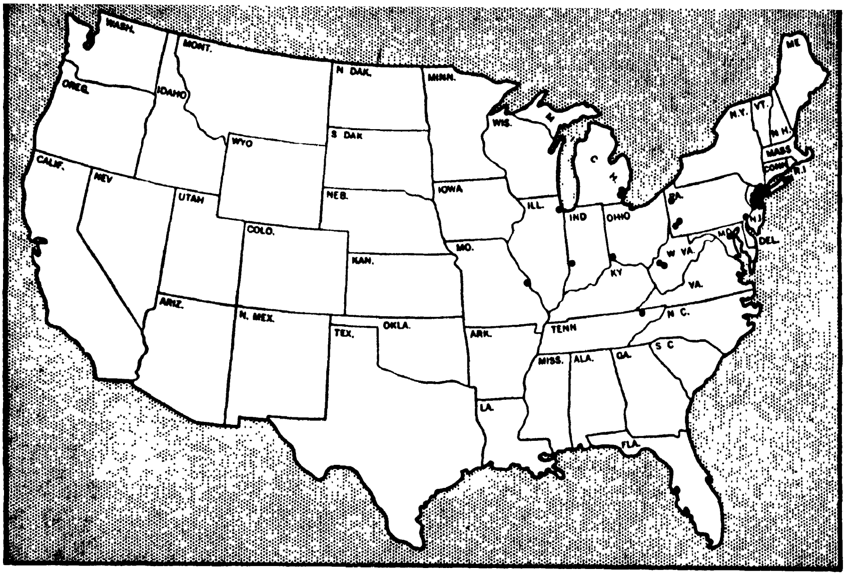
Economic Aspects

The dialkyl phthalates have been used for a number of years as plasticizers with the butyl, amyl, and ethyl esters preferred in the order named. Military demands, for dimethyl phthalate as an insect repellent, for dibutyl and diethyl phthalates as plasticizers for propellants, and for diethyl phthalate as a plasticizer for cable sheathing, were responsible for the sharp production increases during World War II. The use of dimethyl phthalate as an insect repellent was developed during the war and will probably keep production of this material at higher than prewar level. Three different dioctyl phthalates are currently manufactured and are increasingly in demand as plasticizers.

As an insect repellent, dimethyl phthalate must compete with indalone (said to be more effective against biting flies) and ethyl hexanediol (more effective against mosquitoes). Dimethyl phthalate is said to be the most effective of the three against chiggers. Mixtures of the three repellents were used by the Armed Forces during the war. Toward the end of World War II, dimethyl phthalate was being partially replaced as an insectifuge by dibutyl phthalate and benzyl benzoate.

Future production of the other phthalates will depend primarily on production of vinyl plastics in which the various phthalates are widely used. The chief competing materials in the general plasticizer field are the trialkyl phosphate esters (see *Tricresyl Phosphate*), various glycol ethers and ether esters, and alkyl sebacates.

Plants can be so designed that any one of the phthalate esters may be made in the same equipment, thus giving flexibility to production. Batch production is usual. A plant of 1,000,000 lb annual capacity is the minimum economic size. Most plants have capacities between 3,000,000 and 5,000,000 lb annually with the larger ones estimated at 10,000,000 to 15,000,000 lb capacity. An estimated investment cost of $30,000 to $35,000 per 1,000,000 lb annual capacity is required for plants in the 5,000,000- to 10,000,000-lb range.



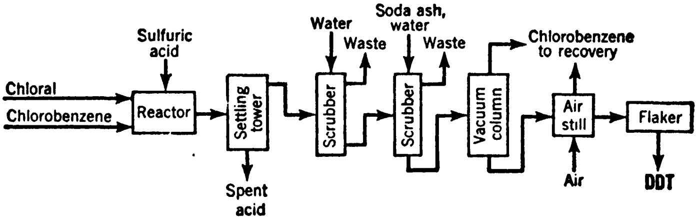
Location of Dialkyl Phthalate Plants

DDT

(DICHLORODIPHENYLTRICHLOROETHANE)

$CCl_3CH(C_6H_4Cl)_2$

From Chloral and Chlorobenzene



Reaction

$$CCl_3CHO + 2C_6H_5Cl \xrightarrow{H_2SO_4} CCl_3CH(C_6H_4Cl)_2 + H_2O$$

90–95% yield

Material Requirements

Basis—1 ton DDT (technical)

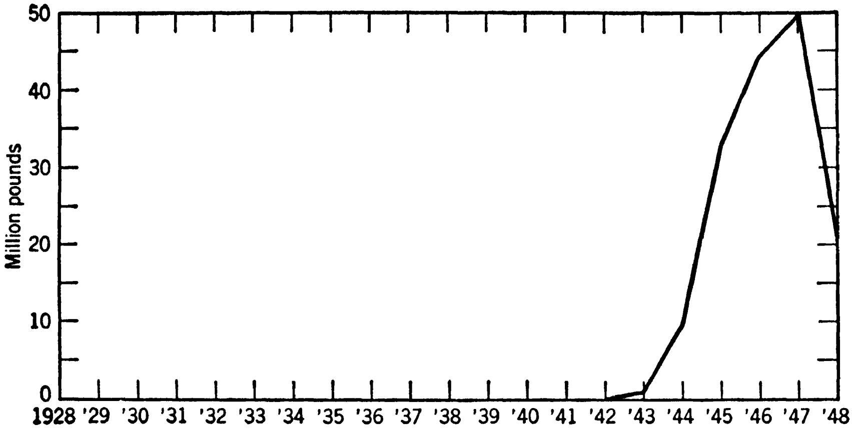
Chloral	890 lb	Sulfuric acid (99%)	9,000 lb
Chlorobenzene	1,800 lb	Sodium carbonate	40 lb

Process

Dichlorodiphenyltrichloroethane [2,2-bis(parachlorophenyl)-1,1,1-trichloroethane] known as DDT is produced by the reaction of monochlorobenzene and chloral or chloral hydrate in the presence of a dehydrating agent: sulfuric acid.

Chloral, chlorobenzene, and concentrated (95 to 99 per cent) sulfuric acid or oleum are charged into an acid-proof lined reactor. The weight ratio used is about 1 part of chloral to 2 parts of chlorobenzene plus 10 parts of 99 per cent sulfuric acid. The temperature is partially controlled by the gradual addition of the reactants. Generally, chloral and chlorobenzene are mixed together with part of the concentrated sulfuric acid. The remaining sulfuric acid or oleum is then added slowly to the mixture. External cooling, or cooling by means of internal coils, is generally necessary to maintain proper reaction temperature (15 to 30°C). The batchwise reaction takes about 5 to 6 hr; it may also be run continuously by using a number of reactors in series.

At the end of the reaction, the DDT-bearing mixture is run into settling towers where the spent acid separates. This acid contains small amounts of sulfonated chlorobenzene and chloral. The recovered acid is purified and concentrated for re-use. The DDT liquor is run from the top of the settling tower to a scrubber where water is used to remove mechanically entrained sulfuric acid. The liquor is then washed with dilute sodium carbonate solution in the second scrubber and finally with water. The tower and scrubber are maintained at sufficiently high temperatures to prevent DDT crystallization.



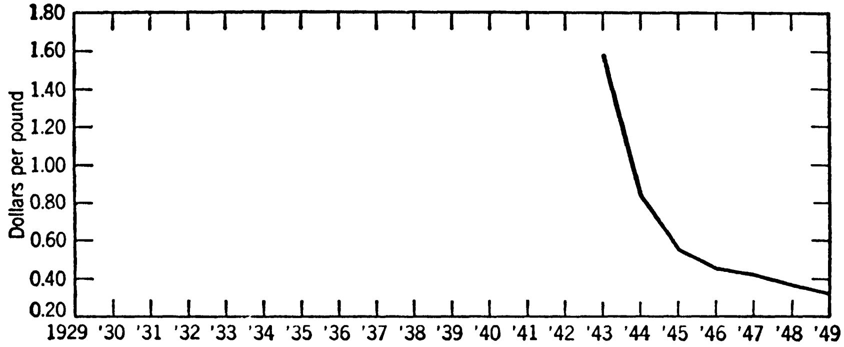
Production—DDT

The neutralized DDT-containing chlorobenzene is run to a column where it is vacuum-distilled at approximately 35 mm absolute pressure and 105°C. The chlorobenzene distillate is passed through a separator and condenser and is finally pumped to storage for recycling. The molten DDT effluent containing 3 to 4 per cent chlorobenzene is pumped to an air-flush still where the chlorobenzene content is further reduced by continuous atmospheric air distillation. The melt is maintained at a temperature about 105°C to prevent crystallization.

The chlorobenzene-free DDT melt is run to a flaker (consisting of a chilled drum rotating through a steam-heated feed trough) where it is chilled to about 85°C. The flaked DDT is then pulverized to the proper mesh size and either packaged in concentrated form or blended with inert extenders. The yield of technical DDT based on the chloral is approximately 95 per cent by weight. The technical material has a setting point of about 88°C. Purified DDT has a setting point of 107 to 108°C. It is made by recrystallization of technical DDT from an appropriate solvent.

Use Pattern

Insecticide and miticide	100 per cent



Price—DDT

Miscellaneous

Properties. Colorless crystals or white odorless powder.

Mol. wt.	354.5	M.P.	107 to 108°C
Density	1.6 g per ml	B.P.	Decomposes

Soluble in alcohol (4 g per 100 g), benzene (106 g per 100 g), kerosene (11 g per 100 g), "Freon," acetone, and most common hydrocarbon solvents at room temperature. Insoluble in water.

Grades. Technical, of various specifications, containing a mixture of several isomers and reaction by-products. Main constituent is 2,2-bis(*p*-chlorophenyl)-1,1,1-trichloroethane. Purified.

Containers and Regulations. Fiber drums, tins, and bottles. No ICC shipping label required.

Economic Aspects

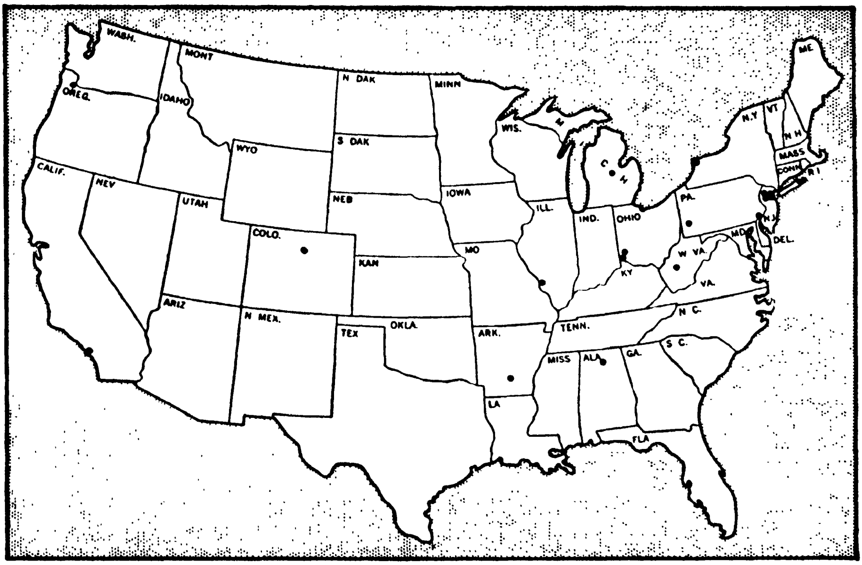
The insecticidal action of DDT must certainly be considered one of the most important chemical discoveries of World War II. Furthermore, few chemicals, outside the medicinal field, have caught the public fancy in a shorter time than DDT. In fact, its popularity has not been an unmixed blessing. A great deal more research must be done to learn its limitations, since an insecticide lethal to harmful insects may also be lethal to insects helpful to man. The extent of the development of DDT resistance among insects must also be determined. There is little doubt, however, that DDT has a place as a household insecticide when mixed with pyrethrum. The latter material has the property of "quick knockdown" not possessed by DDT. For control of bedbugs, DDT is a "natural"; it also has been widely used for mosquito control. It is too early to say how wide a use DDT will have in the insecticide field and whether or not it will be replaced partially by cheaper insecticides more selective in their action. It has, however, displaced arsenicals to a great extent in the spraying of apples and tomatoes, even though difficulty is encountered in washing it off the fruit before marketing.

Toward the end of World War II, the British developed benzene hexachloride (BHC), which supposedly was equal or superior to DDT, particularly against cotton insects. The material is said to be much less toxic to warm-blooded animals than DDT. Recent practice, however, has been to use a mixture of DDT, BHC, and sulfur for cotton insect control. This field affords an excellent example of the progress in organic insecticides since the war. In Texas alone in 1948 over 30,000,000 lb of cotton insect poisons were used. These insecticides were largely DDT, BHC, and Toxaphene (a chlorinated camphene). In fact, cotton insect control is probably the major outlet for both BHC and Toxaphene, although large quantities of the latter have been used for grasshopper control. In 1948 the approximate production of the afore-mentioned insecticides was: DDT, 20,000,000 lb; BHC, 18,000,000 lb; Toxaphene, 13,000,000 lb. Which one will prove the most popular in the next few years is debatable, but production of all three will probably increase.

A number of other insecticides have also entered the market since the war. One of these is chlordane, a superior material for the control of locusts, crickets, ants, and cockroaches. More recently DFDT (difluorodiphenyltrichloroethane) has become available and is said to overcome some of the disadvantages of DDT. Bis(methoxyphenyl)trichloroethane (methoxychlor) has also replaced DDT for some uses. A great deal is expected from lindane, the gamma isomer of BHC, which is the active constituent of commercial BHC in which it is present only to the extent of 12 per cent. The entire organic insecticide field appears to be far from stabilized, and the extent to which and direction in which it will go are still debatable. When it is realized that weeds, insects, and fungi cost the American farmer $5,000,000,000 to $10,000,000,000 per year, one can see that there is still plenty of leeway for development of control methods.

The manufacturing process for DDT has been standardized with respect to raw materials but not with respect to operating variables. The interrelationship of time, temperature, and acid concentration is such that no two manufacturers use exactly the same conditions. The working up of the reaction mass is also subject to considerable variation, and the method varies with economic conditions at each plant. The process as a whole is usually carried out batchwise; some experimentation has been done on continuous processes. Production is aimed toward the para–para isomer, which carries the insecticidal properties, but the commercial product always contains some of the ortho–para, and ortho–ortho isomers. The purified product is, of course, almost entirely para–para.

Economic plant size has not yet been determined, and actual plants vary considerably in size from very small simple installations to large completely instrumented plants of several million pounds annual production. Plant cost is usually estimated at 10 to 15 cents per pound annual production. Because DDT is a new and popular chemical, a wide variety of firms have installed manufacturing units, but in the long run those with the best raw-material position will probably prevail.

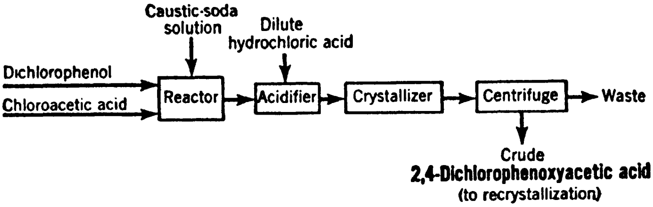


Location of DDT Plants

2,4-DICHLOROPHENOXYACETIC ACID
(2,4-D)

$Cl_2C_6H_3$—O—CH_2COOH

From Dichlorophenol and Monochloroacetic Acid



Reaction

$$Cl_2C_6H_3OH + ClCH_2COOH + NaOH \rightarrow$$

$$Cl_2C_6H_3—O—CH_2COOH + NaCl + H_2O$$

80–85% yield

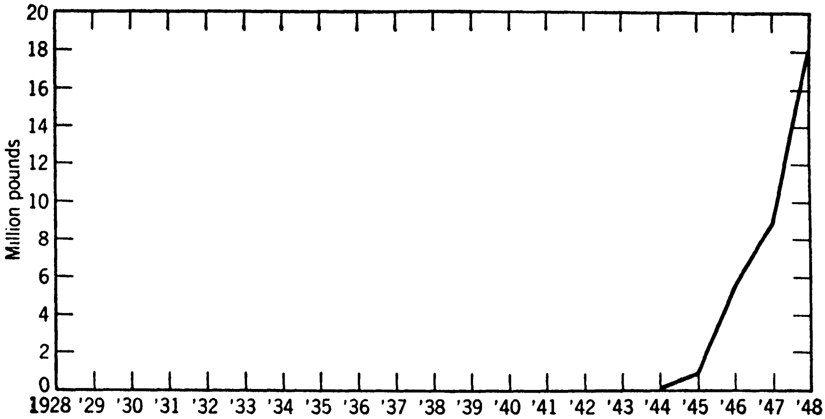
Material Requirements

Basis—1 ton 2,4-dichlorophenoxyacetic acid

2,4-dichlorophenol	1,830 lb	Sodium hydroxide	990 lb
Monochloroacetic acid	970 lb	Hydrochloric acid (18°Bé)	1,750 lb

Process

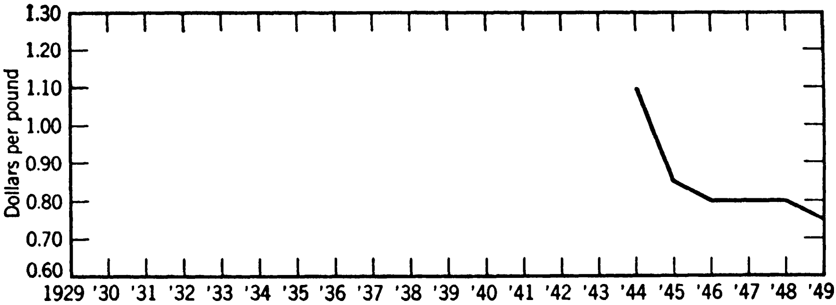
Equimolecular quantities of 2,4-dichlorophenol and monochloroacetic acid are charged to a steam-heated closed kettle along with 2.2 moles of sodium hydroxide as a 15 per cent water solution. Reaction is carried on for several hours under reflux conditions, after which time the reaction mass is acidified with dilute hydrochloric acid. The acidified liquor is sent to a crystallizer and thence to a centrifuge. The crude crystals must then be recrystallized from a suitable solvent, for example benzene, and washed and dried.



Production—2,4-Dichlorophenoxyacetic Acid (Including sodium salt)

Use Pattern

	Per cent
Weed killer	95
Other agricultural uses	5
	100



Price—2,4-Dichlorophenoxyacetic Acid

Miscellaneous

Properties. Colorless, odorless crystals.

Mol. wt. 221.05 M.P. 138°C

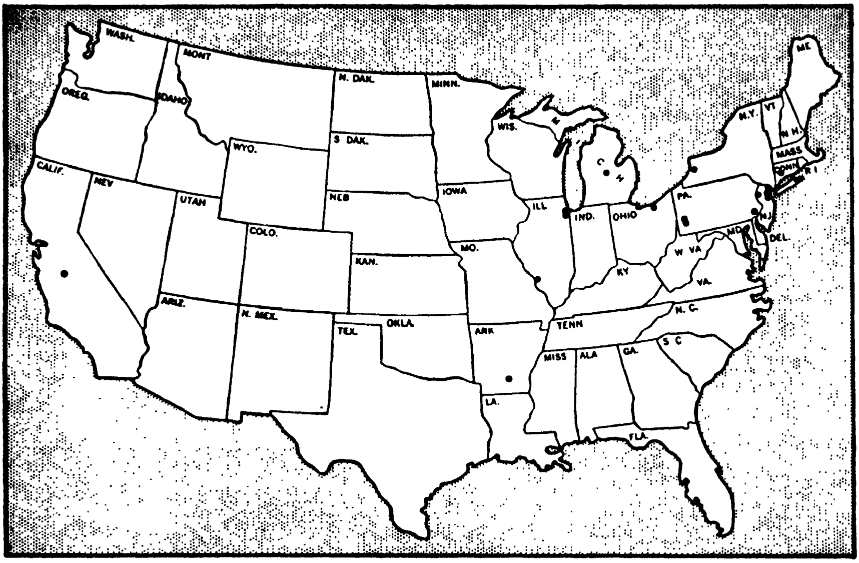
Insoluble in water.

Grades. Technical.

Containers and Regulations. Fiber drums (100 lb). No ICC shipping label required.

Economic Aspects

The rapid increase in production and consumption of 2,4-dichlorophenoxyacetic acid (2,4-D) and its salts and esters since World War II has been one of the striking chemical advances in the postwar era. Those familiar with the field predict that production will ultimately reach 100,000,000 lb annually. It may be, however, that more selective weed killers will be developed, with the consequence that 2,4-D production will level off at a lower figure than predicted. Certainly the need for selectivity is apparent. One recently developed weed killer with high selectivity for sagebrush and poison ivy is 2,4,5-trichlorophenoxyacetic acid.

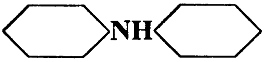


Location of 2,4-Dichlorophenoxyacetic-Acid Plants

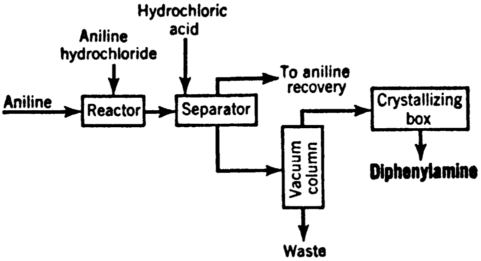
The most important derivatives of 2,4-D at present are the sodium and triethanolamine salts and the isopropyl and butyl esters. Here, again, the field is wide open for more effective formulations. At present, the various ester formulations are the most toxic toward weeds; the sodium salt is most often used as a selective weeding agent; and the amine salt is intermediate in action between the other two forms. In practice, the material is usually applied as a 0.1 per cent aqueous solution (300 gal per acre on large plants and in fields; 200 gal per acre on lawns). Like most new chemicals, some instances of improper use have tended to slow down its acceptance. It is obvious, of course, that care must be used in practice to avoid the killing of valuable plants. Comparatively small quantities are used as a plant hormone, such as in the stimulation of the production of seedless fruit.

Manufacturing plant requirements are comparatively simple. Initial production has been largely taken over by manufacturers of DDT, possibly to round out and consolidate the position of the various companies in the agricultural chemical field.

DIPHENYLAMINE



From Aniline



Reaction

$$C_6H_5NH_2 + C_6H_5NH_2 \cdot HCl \longrightarrow C_6H_5NHC_6H_5 + NH_4Cl \quad \text{or}$$

$$2C_6H_5NH_2 \xrightarrow{\text{Catalyst}} C_6H_5NHC_6H_5 + NH_3$$

80–85% yield

Material Requirements

Basis—1 ton diphenylamine

Aniline	2,650 lb
Hydrochloric acid (20°Bé)	1,700 lb

Process

Diphenylamine is produced by heating aniline under pressure in the presence of a catalyst. Ammonia is liberated during the course of the reaction, at the end of which it may be present in either a fixed or a free state. The reactor, consisting of a corrosion-resistant autoclave, may be operated in either a batch or a continuous manner.

In the batch process, aniline is charged into a closed cast-iron autoclave. Aniline hydrochloride, previously prepared by treating aniline with hydrochloric acid, is added. A ratio of about 1.1 parts of aniline per part of aniline hydrochloride is generally employed. The autoclave is heated to a temperature of 210 to 240°C and is maintained at a pressure of about 90 psi. Generally, 20 to 22 hr are required for an optimum yield. At the end of this time, the reactor contains a mixture of diphenylamine, ammonium chloride, and unreacted aniline.

A catalyst, consisting of a mixture of ferrous chloride and ammonium bromide (ratio 1 to 2 moles), may be used instead of aniline hydrochloride. A glass-lined autoclave is charged with aniline, and about 2.5 per cent of the catalyst is added. The reactor is heated at 310 to 340°C for about 20 hr. The resulting product contains about 74 per cent diphenylamine plus ammonia, unreacted aniline, and catalyst (ferrous chloride–ammonium bromide).

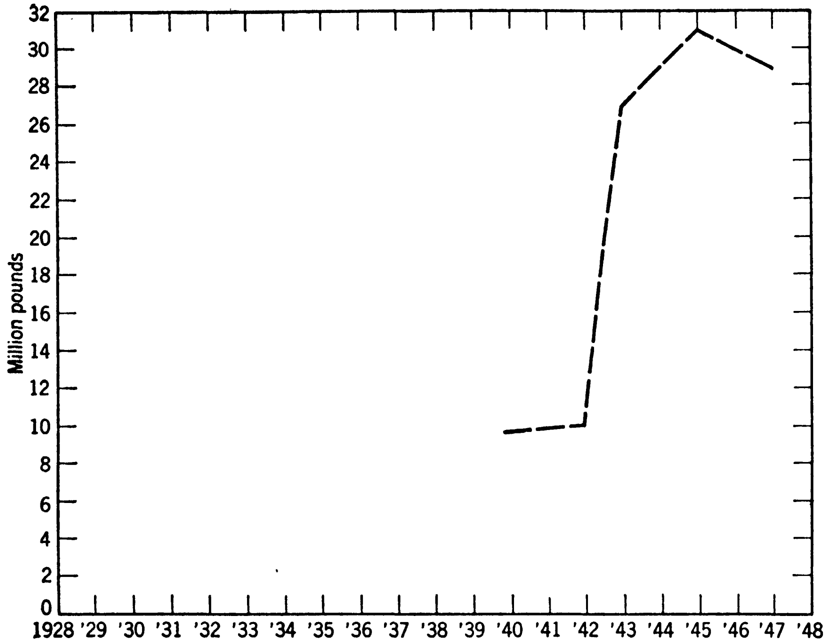
For continuous production, a long, tubular reaction vessel of a corrosion-resistant alloy may be used. The reactor is fitted with a series of reflux columns, is fed from a storage tank at one end, and discharges through a product trap at the other.

Aniline, containing about 5 per cent of a soluble catalyst (consisting of equimolar proportions of ferrous chloride and aniline hydrochloride) is metered from the storage tank into the reactor. A pressure of 200 to 225 psi is maintained on the system by the influx of nitrogen. At a temperature of 300 to 325°C (maintained by a firebox or electric coils), the aniline mixture boils. The vapors are condensed and refluxed back into the reactor. Ammonia is evolved during the reaction and is released from the system by purging at intervals. The reaction mixture proceeds down the length of the reactor and increases in diphenylamine concentration. The flow is regulated so that a period of about 2 hr is required for the material to pass through the reactor. The product, collected in the trap, contains about 40 per cent diphenylamine. After separation, the recovered aniline is recycled.

The recovery of diphenylamine from the reaction mixture is essentially the same in the three previously described processes. The reaction product, containing excess aniline and ammonia (or salt), is discharged from the reactor into a separator (at a temperature of about 60°C). Warm dilute hydrochloric acid is added, which converts the aniline into the water-soluble salt: aniline hydrochloride. The two layers that form are separated by decanting the top, aqueous layer containing ammonium chloride, aniline hydrochloride, and catalyst (if ferrous chloride or ammonium bromide were used). The aqueous solution is run to recovery units, where the aniline is recovered either in the free state or as the salt.

The bottom, oily layer containing the feebly basic amine is discharged from the separator into distilling columns. The crude amine is distilled under vacuum and collected in a receiving box, in which it crystallizes.

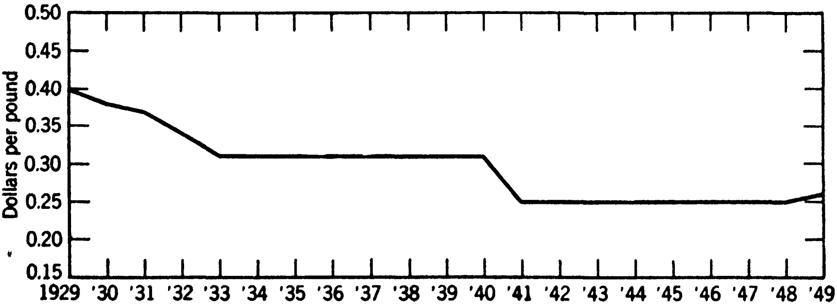
A yield of about 82 per cent based on the weight of aniline charged is realized when a batch reactor and aniline hydrochloride are used.



Production—Diphenylamine (Estimated, not including military production)

Use Pattern

	1947 (est.), per cent
Rubber chemicals	70
Phenothiazine and other parasitides	20
Dyestuffs and miscellaneous	10
	100



Price—Diphenylamine

Miscellaneous

Properties. Colorless to grayish crystals.

Mol. wt.	169.22	M.P.	52.9°C
Sp. gr.	1.160 20°C/20	B.P.	302°C

Soluble in ethyl alcohol (56 g per 100 g at 19.5°C), methanol (58 g per 100 g at 19.5°C), ether, acetone, and carbon disulfide. Very slightly soluble in water.

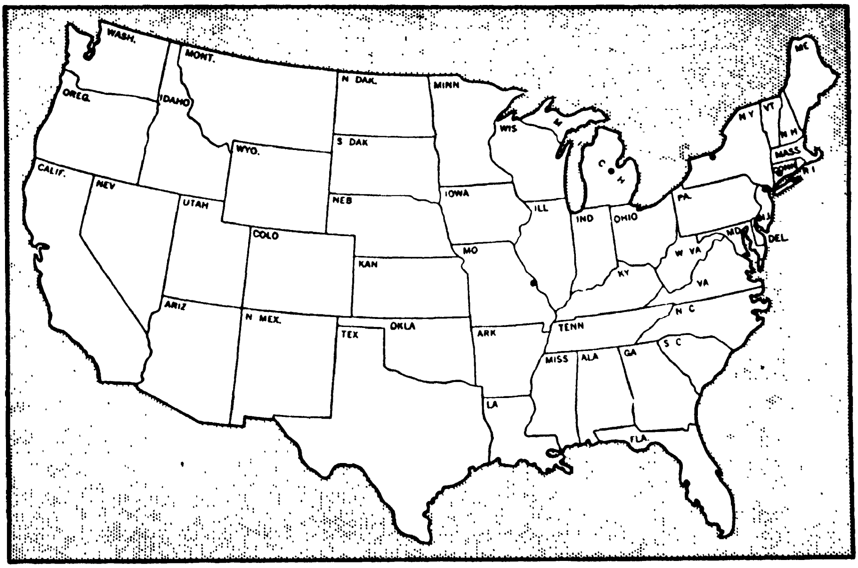
Flash point (closed cup)	307°F
Vapor density (air = 1)	5.82

Grades. Technical.

Containers and Regulations. Barrels and bottles. No ICC shipping label required.

Economic Aspects

Diphenylamine is another chemical for which production soared markedly during World War II. The primary application was as a stabilizer in smokeless powder. This use, in addition to demand by the synthetic-rubber industry (as an accelerator) and by manufacturers of the parasitide, phenothiazine, was responsible for the increased requirements. Most of this production was supplied by Ordnance plants or by manufacturers of dye intermediates who were prewar manufacturers of diphenylamine or similar products.



Location of Diphenylamine Plants

Demand for smokeless powder has, of course, decreased markedly, but the other uses of diphenylamine should increase. Increased production of phenothiazine appears to be a certainty, with attendant increased demand for diphenylamine as a raw material. The use of diphenylamine itself as an ingredient of smears for the control of screwworms is also increasing.

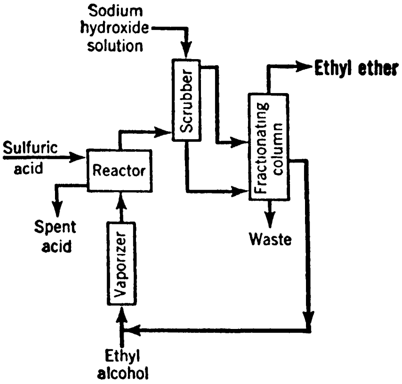
Production of diphenylamine is not complicated, and plants in the range of 1,000,000 to 5,000,000 lb annual production should require an investment of only $100 per 1,000 lb annual production.

ETHER

(ETHYL ETHER)

$C_2H_5OC_2H_5$

From Ethyl Alcohol by Dehydration



Reaction

$$C_2H_5OH + H_2SO_4 \rightarrow C_2H_5HSO_4 + H_2O$$

$$C_2H_5OH + C_2H_5HSO_4 \rightarrow C_2H_5OC_2H_5 + H_2SO_4$$

94–95% yield

Material Requirements

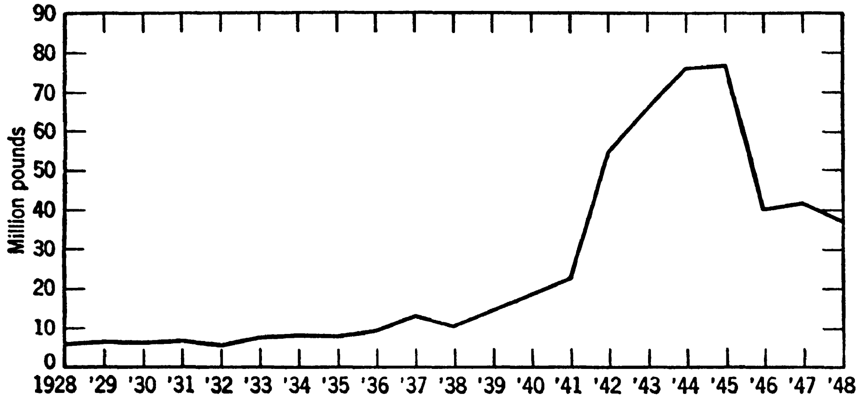
Basis—1 ton ether

Ethyl alcohol (95%)	2,770 lb
Sulfuric acid (66°Bé)	30–50 lb

Process

Concentrated (66°Bé) sulfuric acid and 95 per cent ethyl alcohol are charged into a lead-lined steel reaction kettle. Generally, about 3 parts of acid are charged per part of alcohol. The mixture is heated to 125 to 140°C by means of a steam jacket or internal steam coils. In this temperature range, the reaction is initiated. Vaporized alcohol is allowed to flow into the reactor at a rate determined by the reaction temperature; that is, the rate of alcohol and steam is adjusted so that the temperature is maintained at approximately 127°C.

A mixture of ether, alcohol, and water distils from the reactor and passes to a scrubber. The vapors pass countercurrently to a slow-moving stream of dilute sodium hydroxide solution, which removes mechanically entrained sulfuric acid as well as any acidic reaction products. The alkali solution containing small amounts of ether and alcohol passes from the bottom of the scrubber to the lower section of a fractionating column. Here, the alcohol and ether are removed, and the water is discharged to waste.



Production—Ethyl Ether (Technical, absolute, and USP)

The vapors from the top of the scrubber consist of a mixture of ether, alcohol, and water. They are run to a continuous fractionating column, where separation takes place. Water passes from the bottom of the column to waste. Ethyl alcohol, containing about 5 per cent water, is withdrawn from the center section of the column and returned to the alcohol vaporizer for recycle. Ether vapors pass from the top of the column through a reflux condenser maintained at 34°C. Fractions boiling above this temperature are returned to the column while the ether vapors are condensed and run to storage. This technical or concentrated ether contains very small amounts of alcohol, water, aldehydes, peroxides, and other impurities. The more refined grades, such as ether for anesthesia, are obtained from the technical-grade ether by redistillation and dehydration, followed by an alkali or charcoal treatment.

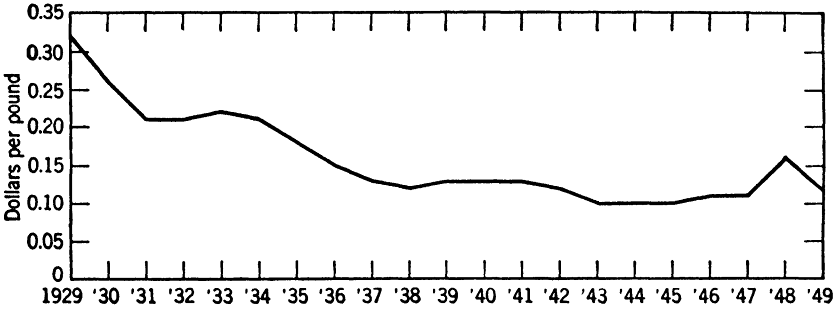
This process is practically continuous and may be run for months before recharging with sulfuric acid. Side reactions, which form tarry products, as well as reduction of some of the sulfuric acid with evolution of sulfur dioxide, necessitate periodic recharging. The yield of technical ethyl ether is 94 to 95 per cent based on the weight of ethyl alcohol processed.

Ethyl ether is also produced in the hydration of ethylene to ethyl alcohol. The first phase of the reaction involves the low-temperature reaction of ethylene and sulfuric acid to give ethyl sulfate ($CH_3CH_2 \cdot HSO_4$). This material yields ethyl alcohol on hydrolysis, which may react with some of the ethyl sulfate to form ethyl ether. For details on the production of synthetic alcohol see *Ethyl Alcohol.*

In yet another process alcohol is vaporized and passed over a catalyst at 200 to 230°C. One proposed catalyst consists of specially prepared alum. The reaction vapors are condensed and fractionated as described previously. A yield of about 75 per cent of theoretical is reported.

Use Pattern

	1947 (est.), per cent
Medicinals, including anesthesia	20
Chemicals	25
Solvent and miscellaneous	55
	100



Price—Ethyl Ether

Miscellaneous

Properties. Colorless, very volatile, highly flammable liquid with a pleasant, aromatic, ethereal odor and sweetish burning taste.

Mol. wt.	74.12	M.P.	−116.3°C
Sp. gr.	0.708 25°C/4	B.P.	34.6°C

Weight per gallon 6 lb (20°C)

Soluble in alcohol, chloroform, benzene, and petroleum ether. Slightly soluble in water (7.5 g per 100 g at 20°C).

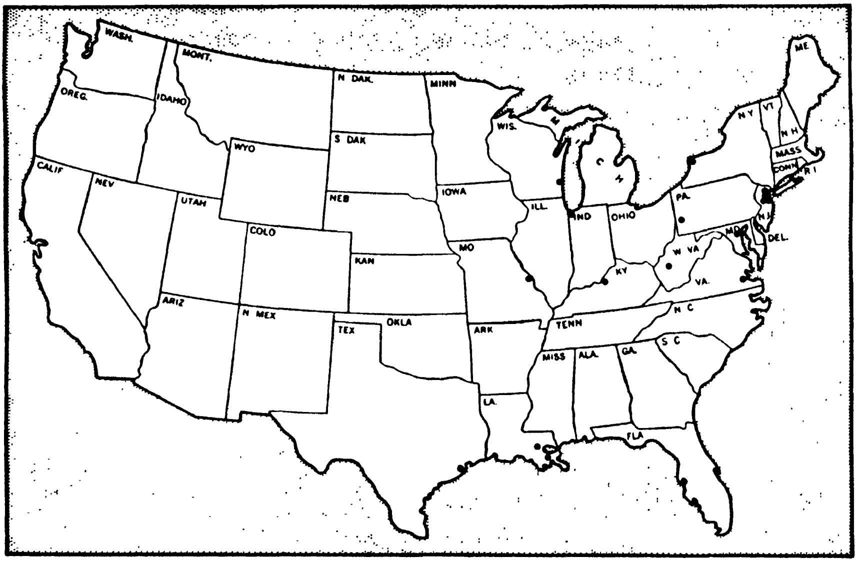
Flash point (closed cup)	−49°F
Ignition temperature	356°F
Vapor density (air = 1)	2.56
Explosive limits (% by volume in air)	Lower 1.85
	Upper 36.5

Grades. USP for anesthesia (unfit for use after 24 hr exposure to air), USP 1880, USP, C.P., concentrated, washed, motor, and anhydrous.

Containers and Regulations. Drums, tins, cans, and bottles. Red ICC shipping label required.

Economic Aspects

Ethyl ether is widely known to the public as the principal anesthetic used in surgery, which use is its best known and most important during peacetime. During World War II, large quantities were used as a solvent in smokeless-powder manufacture, and a lesser amount in butadiene manufacture. In normal times these uses may be expected to be secondary to its anesthetic use. Its other uses are many and varied, but practically all depend on its solvent properties. Wider use as a solvent is limited because of its high volatility and anesthetic properties.



Location of Ether Plants

It has been replaced as a solvent to some extent by isopropyl ether, which is less volatile.

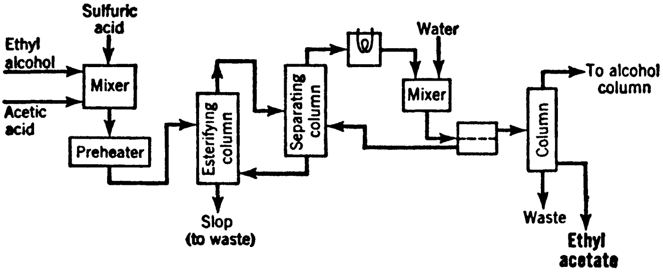
The chief manufacturers of ethyl ether are large pharmaceutical manufacturers and others who make a general line of low-boiling solvents. In the manufacturing process great care must be taken to vent all tanks and other pieces of equipment to a condenser to minimize vapor losses. A hazard also exists during distillation because of the possibility of peroxide buildup. Ether is also obtained as a by-product in the hydration of ethylene to ethyl alcohol and in the manufacture of butadiene from alcohol.

Plant sizes probably vary from 1,000,000 to 15,000,000 lb per yr with the former on the ragged edge of economic plant size. The cost of a plant to manufacture 2,000,000 lb per yr is approximately $25,000.

ETHYL ACETATE

$CH_3COOCH_2CH_3$

From Ethyl Alcohol and Acetic Acid by Esterification



Reaction

$$CH_3CH_2OH + CH_3COOH \xrightarrow{H_2SO_4} CH_3COOCH_2CH_3 + H_2O$$

99% yield

Material Requirements

Basis—1 ton ethyl acetate

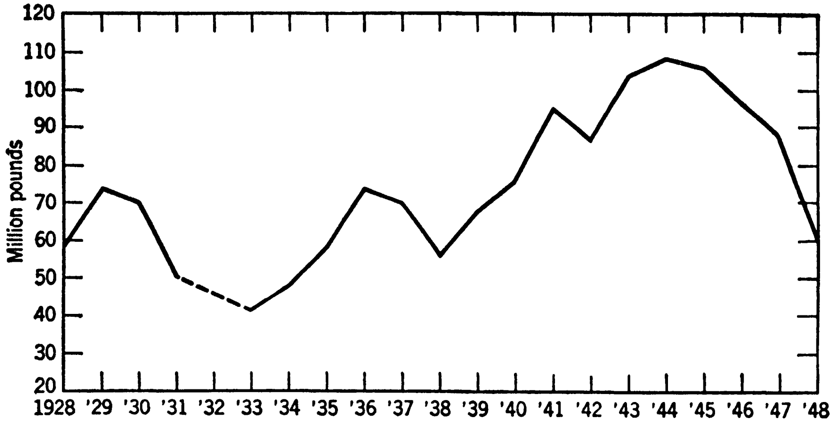
Ethyl alcohol (95%)	1,240 lb
Acetic acid (100%)	1,375 lb
or (8%)	17,250 lb
Sulfuric acid (66°Bé)	15–150 lb

Process

Ethyl acetate is produced by the esterification of acetic acid and ethyl alcohol in the presence of a catalyst such as sulfuric acid. The reaction is reversible and eventually reaches an equilibrium with about a 67 per cent conversion to ethyl acetate. In order to obtain high yields, the reaction must be forced to completion by removing the water formed and employing one reactant in excess. There are many modifications of the process, but all operate on the same general principle; that is, acetic acid is reacted with an excess of ethyl alcohol in the presence of catalytic amounts of sulfuric acid. The process is carried out either batchwise or in a continuous manner, depending on the nature of the raw materials and the size of operation. The main variable is acetic-acid concentration, which may range from very dilute (about 8 per cent) to concentrated (about 80 per cent). Generally, 95 per cent ethyl alcohol and 50 to 66°Bé sulfuric acid are used. The ratio of reactants varies according to the process used and the type of equipment available. For a batch process the reactants may be mixed in the following proportions: 10 parts by weight of 8 per cent acetic acid, 10 parts by weight of 95 per cent ethyl alcohol, and 0.33 part by weight of 50 to 66°Bé sulfuric acid.

The continuous process may be used for any acid concentration,but it is particularly applicable to the utilization of dilute acetic acid, such as that obtained from ethyl alcohol by fermentation. Acetic acid, excess 95 per cent ethyl alcohol, and about 1 per cent of 66°Bé sulfuric acid are mixed and continuously passed through a preheater to an esterifying column. The column and other equipment are generally constructed of copper. The mixture is allowed to reflux, and a suitable amount of distillate is withdrawn from the top of the column which is held at about 80°C. The distillate, containing about 70 per cent alcohol, 20 per cent ester, and 10 per cent water (the acetic acid is consumed in the column) is run to a separating column. Here the mixture is refluxed, and a ternary azeotrope (83 per cent ethyl acetate, 9 per cent ethyl alcohol, and 8 per cent water) is removed from the top of the separating column at approximately 70°C. This homogeneous mixture is run to a proportional mixer, where it is blended with approximately an equal volume of water. The mixture is allowed to settle in a decanter, where the two layers that form are separated. The bottom aqueous layer, containing small amounts of alcohol and ester, is run to the lower part of a separating column. Here the ester is removed in the constant-boiling ternary mixture. The accumulated aqueous alcohol is sent back to the bottom section of the esterifying column where the alcohol is vaporized. The slop containing some sulfuric acid is withdrawn from the bottom of the column to waste.

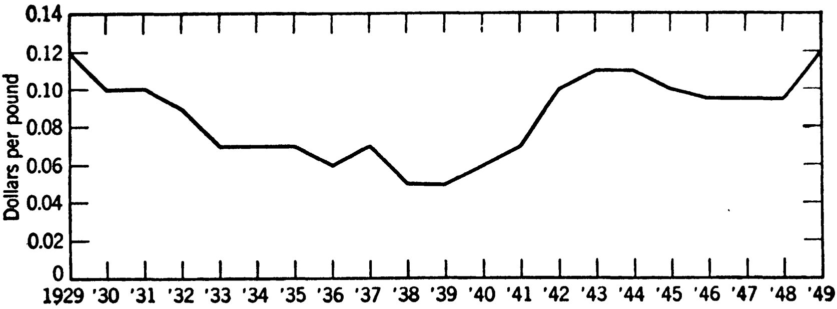
The top layer in the decanter contains about 93 per cent ethyl acetate, 5 per cent water, and 2 per cent ethyl alcohol. This layer overflows to a drying column, where a sufficient amount of the ester is distilled to carry over all the water and alcohol present. This condensate is returned to the separating column for recovery of the ester and re-use of the alcohol. The column residue, containing 95 to 99 per cent ethyl acetate, is withdrawn and either run to storage or redistilled. The latter is generally necessary to remove copper salts formed in the copper columns. Other impurities such as higher-boiling esters may also be present, depending on the purity of the raw materials. The yield of ethyl acetate is 99 to 100 per cent based on acetic acid. Batch process yields are about 95 per cent.



Production—Ethyl Acetate (85%)

Use Pattern

	Per cent
Protective coatings	65
Other solvent uses	20
Chemical manufacture	5
Miscellaneous	10
	100



Price—Ethyl Acetate

Miscellaneous

Properties. Colorless, flammable liquid with a fragrant odor.

Mol. wt.	88.10	M.P.	−82.4°C
Sp. gr.	0.901 20°C/4	B.P.	77.1°C

Soluble in alcohol, ether, and chloroform. Slightly soluble in water (8.5 g per 100 g at 15°C).

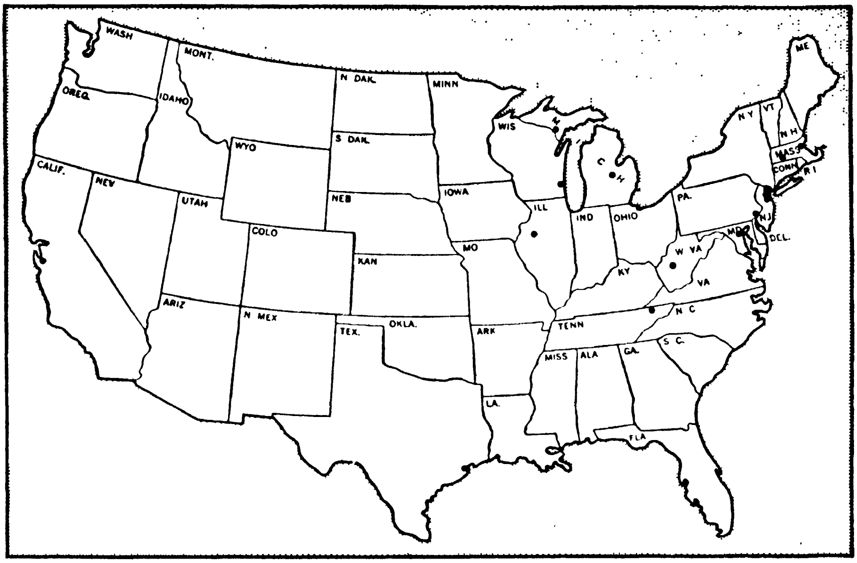
Flash point (closed cup)	24°F
Ignition temperature	800°F
Vapor density (air = 1)	3.04
Explosive limits (% by volume in air)	Lower 2.2 Upper 11.5

Grades. Commercial—85 to 88 per cent, 95 to 98 per cent, 99 per cent, and anhydrous.

Containers and Regulations. Tank cars, drum cars, steel drums, cans, and bottles. Red ICC shipping label required.

Economic Aspects

Compared with butyl and amyl acetates, ethyl acetate is a mass-production item that may be manufactured batchwise but is usually produced by a continuous process. Since it is a low-boiling ester and the product of a fairly rapid reaction, it may be made in a fractionating column where both reaction and product separation take place. Plants vary greatly in size. Batch units are of roughly the same cost as that described for amyl acetate.



Location of Ethyl Acetate Plants

In the past, ethyl acetate production has been a good indication of general industrial activity, chiefly because of the large use of the ester in the protective-coating field. There is no reason to expect markedly different activity in the future.

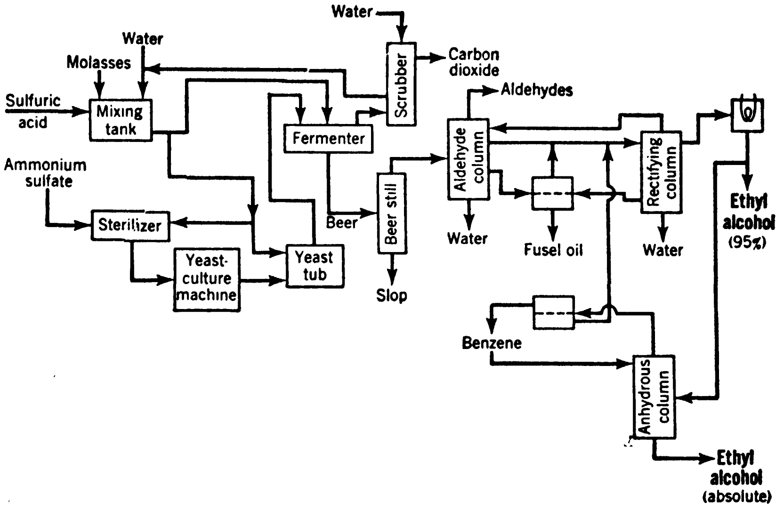
A few manufacturers are making use of the Tischenko reaction to combine 2 molecules of acetaldehyde in the presence of aluminum ethylate. Undoubtedly, more ethyl acetate will be made by this process in the future. β-butylene glycol monoacetate is a by-product of the reaction.

ETHYL ALCOHOL

(ETHANOL, INDUSTRIAL ALCOHOL)

CH_3CH_2OH

From Sugar by Fermentation



Reaction

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Invertase}} 2C_6H_{12}O_6$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

90% yield

Material and Utility Requirements

Basis—1,000 gal 95% ethyl alcohol

(plus 4 gal fusel oil, 4,800 lb carbon dioxide, 1,000 lb carbon, and 900 lb potash)

Molasses (blackstrap)	2,400 gal	Process water	10,000 gal
Sulfuric acid (60°Bé)	170 lb	Cooling water	42,000 gal
Ammonium sulfate	15 lb	Electricity	110 kw-hr
Steam	50,000 lb		

Process

Ethyl alcohol is produced from sugar-containing materials such as molasses by a fermentation process utilizing yeast enzymes to convert the sugar into alcohol.

The most widely used raw material is blackstrap molasses. This is the waste sirup (mother liquor) remaining after the extraction of crystallized sugar from the evaporated sugar-cane juice obtained in commercial cane-sugar mill operations. It contains about 55 per cent total sugar by weight, of which 35 to 40 per cent is sucrose and 15 to 20 per cent is invert sugar (glucose and fructose). High-test molasses, which is evaporated raw sugar-cane juice from which no sugar has been removed and in which the sugar has been largely hydrolyzed to invert sugar with acid, is also used as a raw material. This molasses contains 70 to 80 per cent sugar, of which 22 to 27 per cent is in the form of sucrose and 50 to 55 per cent is invert sugar. Only very small amounts of sugar-beet molasses are utilized for the production of alcohol in the United States. It contains from 48 to 52 per cent sucrose with practicallly no invert sugar.

Blackstrap or high-test molasses is charged into a mixing tank, where it is diluted with sufficient warm water to give a sugar concentration of 10 to 15 per cent. Sulfuric acid is added to reduce the *p*H of the molasses from about 5.3 to between 4.0 and 5.0, depending on plant practice. Most of the blackstrap molasses does not require the addition of nutrients. However, high-test molasses requires considerable quantities of ammonium sulfate and other salts such as phosphates. The nonsugar solids nutrient content of high-test molasses is about 7 per cent, compared to 28 to [illegible] t found in blackstrap molasses.

The diluted a [illegible] olasses, called mash, is run into large wooden or steel ferment [illegible] aks where a selected strain of yeast is added. The yeast charge, previously grown by inoculating sterile mash under controlled conditions, is added with the mash charge to the extent of about 5 per cent. In the fermenters reaction takes place at 70 to 88°F. Since the reaction is exothermic, cooling coils or sprays are generally used. However, near the end of the fermentation, the temperature may be as high as 100°F. The fermentation requires 28 to 72 hr (average about 45 hr) to produce an alcohol concentration of 8 to 10 per cent. The yeast supplies the enzyme, invertase, which catalyzes the hydrolysis of sucrose and produces the enzyme, zymase, which converts the monosaccharide to alcohol and carbon dioxide. The latter is vented during the reaction or recovered. If the carbon dioxide is to be recovered, the gas is scrubbed with water to remove entrained alcohol (0.5

to 1 per cent of the total) and purified, using activated carbon or strong oxidizing solutions. For details see *Carbon Dioxide.*

After the fermentation reaction is completed, the liquor, now known as beer and containing 8 to 10 per cent alcohol, is withdrawn from the fermenters, passed through heat exchangers, and pumped to the upper sections of a beer still. The alcohol and other volatiles such as aldehydes are distilled off. The residue, known as slop or stillage, is discharged from the bottom of the still through a heat exchanger. The slop may be run to waste, or it may be evaporated and used as a constituent in cattle feeds, since it contains proteins, residual sugars, and vitamin materials. Frequently, the slop is concentrated and used as a core binder in foundries or as a briquet adhesive. It may be dried, calcined, and extracted to yield activated carbon and potash fertilizer.

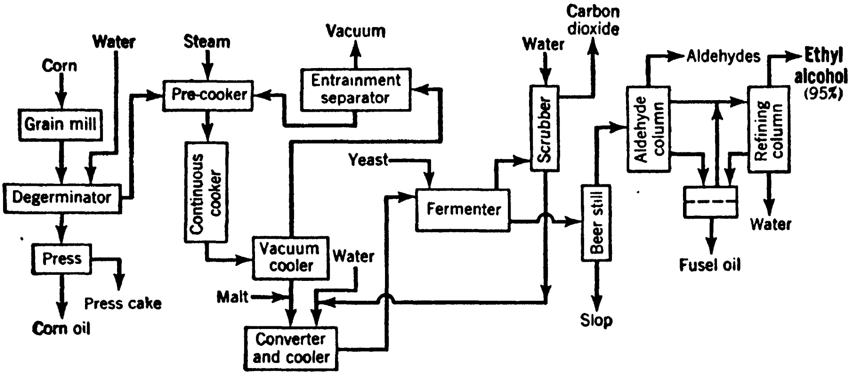
The overhead from the beer column is passed through a heat exchanger and condensed. This condensate, high wines, contains 50 to 60 per cent alcohol, and is charged into an aldehyde or heads column where aldehydes and other low-boiling impurities are separated as overhead. The effluent from about the middle of the column is run into a rectifying or refining column. The tails from the aldehyde column and the weak fractions from the beer still, called low wines, are rerun with subsequent batches.

In the rectifying column, the heads, which contain a trace of aldehydes, are returned to the aldehyde column. Near the top of the column, the azeotropic alcohol–water mixture of 95 to 95.6 per cent alcohol is taken off, condensed, and run to storage. The higher-boiling alcohols, fusel oils, are withdrawn further down the column. After running through a cooler, the fusel oils are generally fractionated to give amyl alcohol for solvent use. For details see *Amyl Alcohol.* Water is discharged from the bottom of the column.

The 95 per cent ethyl alcohol from the rectifying column, which is obtained in about 90 per cent of the theoretical yield based on the sugar content of the molasses, is stored in Government-bonded warehouses. The alcohol is either sold (tax-free or tax-paid), denatured, or dehydrated. Anhydrous or absolute alcohol is produced by several methods. A third component such as benzene may be added and the mixture distilled. The ternary azeotrope thus formed carries over the water, leaving behind anhydrous alcohol. Another method uses countercurrent extraction with a third component such as glycerine or ethylene glycol. The added component depresses the vapor pressure of the water and allows anhydrous alcohol to be distilled from the top of the extraction column. Both these methods are run, using continuous columns.

Most of the 95 per cent alcohol and the anhydrous alcohol is denatured into one of the three completely denatured formulas or 57 specially denatured formulas.

From Starch by Fermentation



Reaction

$$\underset{\text{Starch}}{[C_6H_{12}O_6]_x} + xH_2O \xrightarrow{\text{Diastase}} xC_6H_{12}O_6$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

90% yield

Material Requirements

Basis—1,000 gal 95% ethyl alcohol

[plus 400 lb corn oil, 10 gal fusel oil, 4,800 lb carbon dioxide, 750 lb press cake, and 4,400 lb stock feed (dry residue)]

Corn	372 bu	Yeast	Variable
Barley malt	83 bu	Process water	17,000 gal

Process

Various types of starchy materials are suitable for the production of ethyl alcohol. Although cereals (corn, oats, grain sorghum, rye, rice, barley, and wheat), potatoes, sweet potatoes, and Jerusalem artichokes have all been used to produce beverage alcohol, only the most abundant grain, corn, and potatoes are used to any extent to produce industrial alcohol.

For the manufacture of industrial ethyl alcohol from corn, the first step comprises grinding the corn in grain mills and removing the oil-bearing germ. In some plants, degermination is not practiced, and the germ passes through the fermentation cycle and is removed with the slop, from which it may be later recovered. In the former process, press cake and corn oil are obtained as by-products, whereas in the latter only corn oil is recovered, or it may be left to enrich the stock feed (dry residue).

The ground corn is then put through a cooking (mashing) and converting (saccharifying) cycle, which gelatinizes the starch and converts it into fermentable sugars. The conversion may be accomplished continuously or batchwise, either enzymes or dilute mineral acids being used. In the enzyme process, malt, produced by the controlled germination of barley, is used as a source of the enzyme, diastase, to catalyze the saccharification. It is also possible to saccharify starch by use of the enzymes produced by molds (the amylo process) or by the aforementioned hydrolysis, utilizing dilute mineral acids, such as hydrochloric or sulfuric.

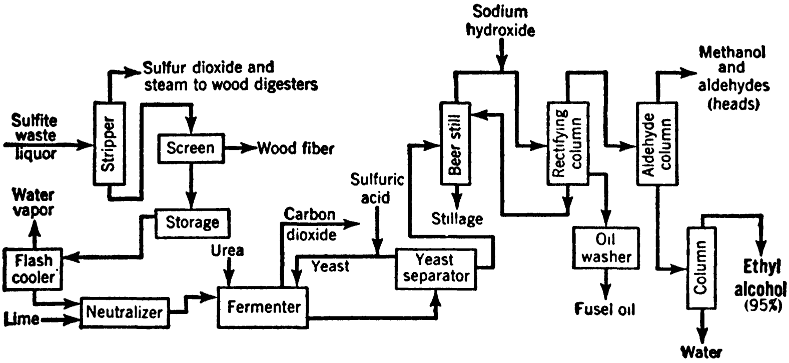
In continuous cooking, the ground grain is slurried in a mixture of water and part of the slop or stillage, which has been recycled. It is then pumped through a heating jet (precooker or paster), where it is mixed with steam at a temperature of 350 to 360°F. The slurry is passed through a pipe coil (cooker) of a length designed to give 1 to 2 min holding time into a vacuum cooler, where the cooked slurry is "flashed" and cooled. It is then mixed with malt and charged into a converter (mash cooler) prior to the fermentation cycle. This procedure is also used for acid hydrolysis, except the dilute mineral acid is added to the grain slurry before cooking and is later neutralized with calcium carbonate just before it is cooled in the "flash" chamber.

The complete operation for the continuous cooler is approximately 6 min compared to the 2- to 4-hr batchwise cooking cycle. When the latter is used, the disintegrated grain is blown into large vats where it is mixed with water and malt (enzymes) or dilute acid. The mixture is heated to about 140°F with sparged steam and is agitated with large rakes. After the required amount of time, the mix is cooled and is ready for the fermentation.

The resulting sugar solution or wort from the cookers, containing 10 to 15 per cent fermentable sugars, is charged to the fermentation tanks and inoculated with yeast. The fermentation takes place at 65 to 85°F, and this and the remainder of the process are in general the same as that previously described for the production of alcohol from molasses.

The only differences lie in the disposition of the slop or stillage and the amount of by-products obtained. The slop is rich in proteins and has a high feed value for livestock, particularly where degermination has not been carried out. This stillage may be concentrated and used in wet form, or it may be dried and sold as distiller's grains. Vitamin concentrates such as riboflavin are also obtained by processing part of the stillage. Besides stock feed, press cake and corn oil are obtained if degermination is practiced. In addition, approximately 2.5 times as much fusel oil is recovered as is produced by molasses fermentation.

From Sulfite Waste Liquor by Fermentation



Reaction

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Material and Utility Requirements

Basis—1,000 gal ethyl alcohol (95%)

[plus 50 gal methanol (80%) and 2 gal fusel oil]

Sulfite waste liquor (1.35% fermentation sugars) ≈ 45 tons sulfite-liquor pulp	125,000 gal	Lime	3,500 lb
		Sulfuric acid	150 lb
		Water	Variable
		Steam	150,000 lb
Yeast (added)	2.5 lb	Electricity	1,500 kw-hr
Urea	62 lb		

Process

Sulfite waste liquor contains sugars derived from wood, which may be converted into ethyl alcohol by fermentation resulting from the action of yeast.

The spent liquor from the manufacture of sulfite wood pulp is known as sulfite waste liquor. In the manufacturing process, wood chips are cooked in an aqueous solution of calcium bisulfite and sulfurous acid for 8 to 10 hr at a temperature of about 135°C and pressures of 80 to 100 psi. During this cooking period, which takes place in large pressure vessels called digesters, the cellulosic fibers are set free. A valve in the bottom of the digester is then opened, and the resulting pulp is blown into blow pits. Here the fibers and liquor are separated by draining or vacuum (vacuum washing), and the fibers are washed. The diluted sulfite waste liquor, which is recovered from the pits in 80 to 90 per cent yield, contains dissolved wood constituents such as lignins and sugars, as well as the spent chemicals of the process. The sugar content, which results from some naturally occurring sugars or is formed by the acid hydrolysis of the hemicelluloses in wood, runs between 2 and 2.5 per cent. Part of these sugars are nonfermentable pentoses, whereas the remainder (1.3 to 1.8 per cent) are fermentable hexoses such as glucose, mannose, and galactose.

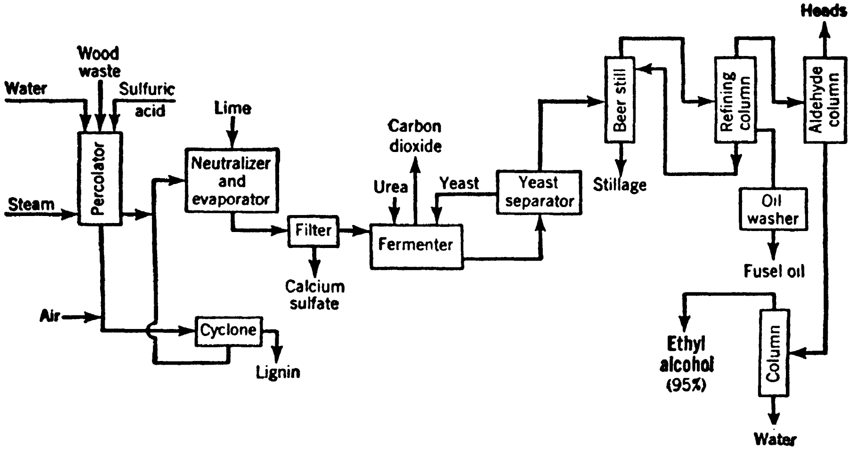
The sulfite waste liquor is obtained from the blow pits at a temperature about 90°C and is pumped to a steam-stripping column. Here the sulfur dioxide is recovered for re-use in the digesters. The hot liquor is pumped over screens to remove residual pulp fibers and is then stored. From storage, the liquor is pumped to flash coolers, where it is cooled to about 30°C by vacuum evaporation, using steam ejectors. The *p*H of the liquor is adjusted (to slightly higher than 6.0) by addition of a lime slurry; urea is added as a nutrient (nitrogen source). No other nutrients such as potash or phosphorus are required. The liquor, thus conditioned and partially concentrated, is pumped into a series of fermentation tanks. Yeast, reclaimed from the previous cycle, is added, and the fermentation is allowed to run about 20 hr. The tanks are equipped with agitators to keep the yeast in suspension; the flow of mash is continuous through the fermenters. Carbon dioxide is produced and is vented or may be recovered by suitable processes (see *Carbon Dioxide*).

The fermented liquor (wort), containing about 1 per cent yeast by volume, is pumped to centrifugal yeast separators, where the yeast concentrate (*ca.* .10 per cent aqueous slurry) is removed, conditioned with sulfuric acid, and returned to the first fermenter for re-use. This separation and recycling of yeast is the essential part of the fermentation procedure (Melle process). Very little fresh yeast is required in continuous operation, and the recycling may be carried out 300 times or more.

The clarified beer, which contains about 1 per cent alcohol by volume, passes through preheaters and is pumped into a beer still. The alcohol is stripped from the beer, and the slop or stillage is recovered at the bottom. The aqueous alcohol is mixed with dilute sodium hydroxide to neutralize the acids present and is then charged into a rectifying column. Here, under substantial reflux, the alcohol is concentrated to about 95 per cent and is fed into an aldehyde column where the low-temperature heads, consisting mostly of methanol (80 to 85 per cent) and aldehydic impurities (about 2 per cent), are removed. The methanol is formed in the digester and is carried through the fermentation process. Fusel oil is obtained in an amount of about 0.2 per cent (based on the ethyl alcohol distillate) from a lower plate in the rectifying column and, after washing, is sent to storage for sale or refining.

The alcohol from the bottom of the aldehyde column is vaporized to remove any residual high boilers and after condensation is sent to storage as 95 per cent ethyl alcohol. The entire process is continuous, and 95 per cent alcohol is obtained in a yield of about 22 gal per ton of sulfite pulp. See alcohol from sugars for operation of the alcohol and by-product recovery processes, denaturation, etc.

From Wood Waste by Hydrolysis and Fermentation



Reaction

$$\underset{\text{Cellulose}}{(C_6H_{10}O_5)_x} + xH_2O \xrightarrow{H_2SO_4} \underset{\text{Glucose}}{xC_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Material and Utility Requirements

Basis—1,000 gal ethyl alcohol (95%)

(plus 13,000 lb lignin, 3,660 lb calcium sulfate, and 43,500 gal spent beer)

Wood waste	39,000 lb	Water	260,000 gal
Lime	2,200 lb	Steam	125,000 lb
Sulfuric acid	2,300 lb	Electricity	90 hp
Urea	60 lb	Compressed air	165 cfm
Yeast (added)	5 lb		

Process

Waste wood in the form of chips, shavings, or sawdust is hydrolyzed by dilute sulfuric acid to yield in successive steps: hemicellulose, α-cellulose, and fermentable sugars. After removal of the hydrolyzate and neutralization of excess acid, the sugars are fermented to ethyl alcohol by the use of yeast.

The wood waste (such as bark-free Douglas-fir shavings), after being shredded to proper size, is charged into a series of vertical cylindrical percolators along with dilute sulfuric acid (0.4 to 0.8 per cent). A ratio of about 8 parts water to 1 part wood with an initial sulfuric-acid concentration of 0.9 per cent is used. Eight to 15 batches of dilute sulfuric acid are allowed to percolate through the wood shavings. An initial steam pressure of 50 psi used on the first batch is gradually increased to 150 psi on the final one. During this time the concentration of the added acid solution is decreased stepwise to a final concentration of about 0.4 per cent. At the end of a 6-hr cycle, the solids, containing mostly lignin, are blown by compressed air into a cyclone. The separated lignin is pressed to reduce the water content to below 50 per cent and is then sent to the boilers to be used as fuel.

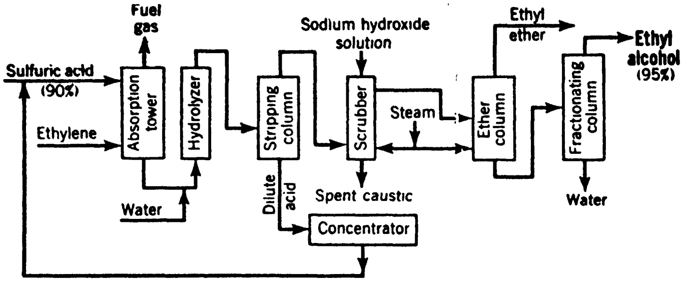
The acid liquor from the percolators is flashed to 35 psi, combined with the liquor from the cyclones, and neutralized with lime to a *p*H of about 5.2. The neutralization is carried out hot to reduce soluble calcium sulfate and to aid the subsequent fermentation. The neutralized liquor is filtered to remove calcium sulfate and is cooled in flash evaporators in stages to a steam pressure corresponding to 150°F.

The resulting wort containing about 6 per cent total sugar, of which over two thirds is fermentable, is charged into fermenters. Here, after cooling to 86°F, the sugars are fermented according to the yeast re-use procedure described under the sulfite waste-liquor process. Nitrogen- and phosphorus-containing nutrients must be added. The fermentation is effected in about 20 hr.

The resulting beer, containing about 2 per cent alcohol by weight, is distilled in the usual manner, as described under the afore-mentioned sulfite-liquor process. The yield of 95 per cent alcohol is 40 to 55 gal per ton of dry wood waste, depending on the amount of bark present.

Claims have been made that 10 to 30 lb furfural and 10 to 20 lb methanol can be recovered as by-products from each ton of wood waste processed.

From Ethylene by Esterification and Hydrolysis



Reaction

$$CH_2{=}CH_2 + H_2SO_4 \rightarrow C_2H_5OSO_2OH$$

$$2CH_2{=}CH_2 + H_2SO_4 \rightarrow C_2H_5OSO_2OC_2H_5$$

$$C_2H_5OSO_2OH + C_2H_5OSO_2OC_2H_5 + 3H_2O \rightarrow 3C_2H_5OH + 2H_2SO_4$$

$$2C_2H_5OH \xrightarrow{H_2SO_4} C_2H_5OC_2H_5 + H_2O$$

Material and Utility Requirements

Basis—1,000 gal ethyl alcohol (95%)

Ethylene	4,000 lb	Water	240,000 gal
Sulfuric acid	500 lb	Steam	20,000 lb
Sodium hydroxide	110 lb	Electricity	2,000 kw-hr
Dowtherm (make-up)	0.5 lb	Fuel	2,800,000 Btu

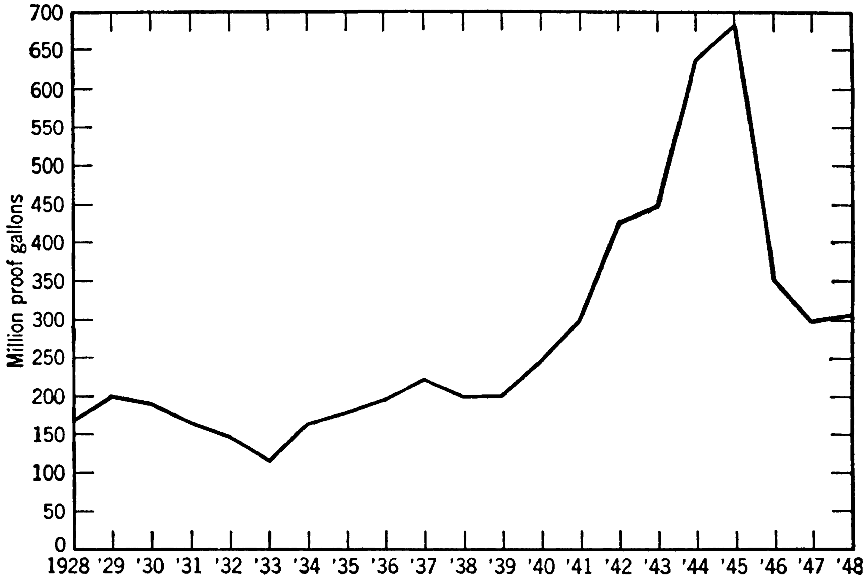
Process

Synthetic ethyl alcohol is produced by absorbing ethylene in sulfuric acid to give a mixture of ethyl sulfates, which are then hydrolyzed to crude ethyl alcohol and dilute sulfuric acid. The alcohol is purified by distillation, and the acid is concentrated for re-use.

Special ethane–propane stock gases are cracked to a high yield of ethylene, which after scrubbing (caustic soda and water) and purifying, serves as the raw material for alcohol. The ethylene is passed into the bottom of an absorber countercurrent to 90 per cent sulfuric acid. The unabsorbed gases pass out the top to be used as fuel. The resulting liquid is a mixture of monoethyl and diethyl sulfates, which are discharged from the bottom of the absorption tower with a small amount of free acid and water. The reaction is exothermic, and the temperature is controlled by the rate of feed of the two reactants.

The mixed esters from the absorber are pumped into the bottom of a hydrolyzer along with a measured volume of water. Here the sulfates are hydrolyzed to ethyl alcohol, dilute sulfuric acid, and small amounts of ethyl ether and other materials. The crude alcohol–acid solution is run into a stripping column, where steam carries over the alcohol, ether, and small amounts of acid. Dilute sulfuric acid is withdrawn from the bottom of the column, cooled, and stored for recovery.

Dilute acid is concentrated for re-use by vacuum evaporation. One process for acid recovery consists of passing the dilute acid through a reboiler, where sufficient water is evaporated to raise the acidity to 70 per cent. The water vapor is returned to the base of the steam generator to be used as a stripping medium, thereby decreasing the steam consumption of the generator. The 70 per cent acid is run into a two-stage vacuum evaporator, where it is concentrated to 90 per cent acid. The two stages are operated at an absolute pressure of 2.5 and 0.4 in. Hg, respectively. The heating medium used is Dowtherm A at about 20 psi, which gives a temperature of approximately 300°C. The concentrated sulfuric acid, which is kept below 190°C during recovery, is cooled and stored for re-use in the ethylene absorber.



Production—Ethyl Alcohol

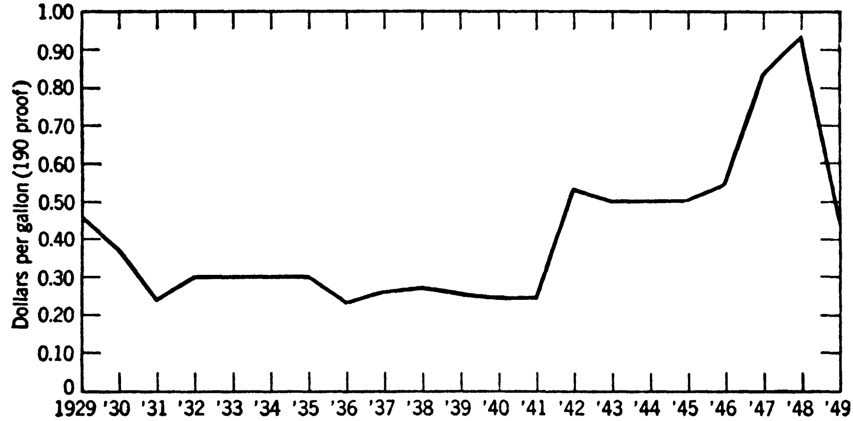
The crude alcohol vapors leaving the stripping column are passed into the bottom of a scrubber where acid carried over by entrainment is neutralized by a countercurrent flow of sodium hydroxide solution. Spent caustic leaves the bottom of the scrubber; the alcohol, ether, and water vapors from the top are condensed and pumped to crude-alcohol storage tanks.

The purification of the crude alcohol is very similar to the procedure used for fermentation alcohol. The crude alcohol is run into an ether column where the ethyl ether is removed by live steam. The alcohol is then passed into a fractionating column where 95 per cent alcohol vapors are condensed and run to storage or denatured for sale. Approximately 1 gal of 95 per cent alcohol is produced from 4 lb of ethylene.

One recent synthetic-alcohol plant uses a high-pressure (1,000-psi) process in which ethylene is directly hydrated to ethyl alcohol with the aid of a phosphoric-acid catalyst. Conversion is quite low, but yields of 95 per cent are claimed.

Use Pattern

	1948 (est.), per cent
Acetaldehyde	37.5
Antifreeze	15
Ethyl acetate and ether	7.5
Miscellaneous chemicals and solvent	40
	100



Price—Ethyl Alcohol

In February 1949 the price of 190 proof S.D.-1 alcohol dropped to 21 cents per gallon

Miscellaneous

Properties. Colorless, fluid liquid of characteristic odor.

Mol. wt.	46.07	M.P.	−112°C
Sp. gr.	0.7905 20°C/20	B.P.	78.3°C

Weight per gallon 6.578 lb (20°C)

One wine gallon 190-proof alcohol = 1.9 proof gallons

Miscible in all proportions with water, ether, chloroform, and a wide variety of organic compounds.

Flash point (open cup)	70°F
Ignition temperature	700°F
Vapor density (air = 1)	1.59
Explosive limits (% by volume in air)	Lower 3.5
	Upper 19

Grades. Pure, 188-proof, 190-proof, 96 per cent, and anhydrous (tax-free or tax-paid); specially denatured (57 formulas); completely denatured (3 formulas); proprietary solvent; proprietary antifreeze solutions.

Containers and Regulations. Tank cars, 55-gal steel drums, 50-gal wooden barrels, 5-gal steel or tin containers, 1.2-gal bottles, 1-gal and smaller metal containers. Red ICC shipping label required.

Economic Aspects

Ethyl alcohol is undoubtedly the political football of the chemical industry. This fact is occasioned primarily by its alternate use in beverages and spirits with attendant high revenue taxes and Governmental regulation. Also, because of potential wide use as an internal-combustion fuel, it has become the star performer of the political chemurgists.

Interprocess competition in alcohol manufacture is of a dual nature: the fermentation versus the synthetic process, and the competition of various raw materials for fermentation.

In comparing various processes, three factors must be considered: capital investment, raw material cost, and operating costs. For purposes of comparison, plants may be divided into five groups: synthetic, grain fermentation, molasses fermentation, sulfite liquor fermentation, and fermentation of hydrolyzed wood. Of these, the primary prewar sources of alcohol were molasses fermentation and synthetic alcohol. Because of the shortage of molasses, large quantities of wheat and granular wheat flour were used as raw materials during World War II (alcohol production soared from a prewar production of 100,000,000 gal yearly to over 600,000,000 gal in 1944, the peak year), chiefly in converted whiskey distilleries. Toward the end of the war, when it appeared that wheat might have to be conserved for food, two sulfite liquor plants were built, and construction of a wood-hydrolysis plant was authorized (completed after the war). Production-wise the last two types of plants are unimportant, but both may be of economic importance in the future.

For fairly large installations (7,000,000 to 10,000,000 gal per yr), plant investment costs per 1,000,000 gal of 190-proof alcohol annually are: synthetic, $425,000; grain, $350,000; molasses, $185,000; sulfite, $475,000; wood, $600,000. The cost of the synthetic plant includes a cracking plant for cracking propane to ethylene. The actual alcohol plant costs much less (about 50 per cent), but refinery streams rich in ethylene are no longer valueless, as has sometimes been assumed.

Raw-material costs vary so much that it is useless to set down specific figures. In prewar economy it was usual to calculate costs based on molasses at 5 cents per gallon and corn at 40 cents per bushel. During the war, blackstrap molasses was available only in limited quantity, and in 1948 its price reached 37 cents per gallon, only to fall to 4 cents in 1949. Low-grade corn, when available, was above 85 cents per bushel. In late 1947 cash corn reached $2.97 per bushel on the Chicago market. At about the same time, molasses sold for 25 cents per gallon. It also appears that the future molasses supply will be limited since sugar millers have devised means of removing more sugar than formerly from the raw juices. Grain prices are notoriously unstable, and little if any grain was used for industrial-alcohol production in prewar years. During the war, as previously mentioned, large quantities of wheat and granular wheat flour were used. Sulfite liquor is usually considered to be free and may even have credited to its use the cost of its disposal. Waste wood for hydrolysis is generally considered to have an average value of $3 per ton, chiefly for transportation. This is true only in the proximity of large saw mills and for wood in excess of that which can be used as fuel.

Conversion costs also vary, but for relative purposes the following figures per gallon (190 proof) may be used: synthetic, 2 to 3 cents; grain, 6 to 7 cents; molasses, 3 to 4 cents; sulfite, 12 cents; wood, 15 to 18 cents. It should, of course, be remembered that credits may be taken for such by-products as fusel oil (4 to 5 gal per 1,000 gal of alcohol) from either blackstrap molasses or corn; 4.8 lb carbon dioxide (99.8 per cent) per gal alcohol (190 proof) in fermentation processes; 5.5 lb by-product feed per gal of alcohol from corn; 0.9 lb potash per gal of alcohol from molasses, methanol (10 per cent of total alcohol production) in the sulfite-liquor process. No credit should be given to the lignin by-product (5 tons per 1,000 gal) of a wood-hydrolysis plant except for its fuel value. Development of an adequate outlet for this material would, however, change the economics of the wood-hydrolysis process markedly. Credit for by-product sulfur dioxide in the sulfite-liquor process has been considered in calculating the conversion cost shown.

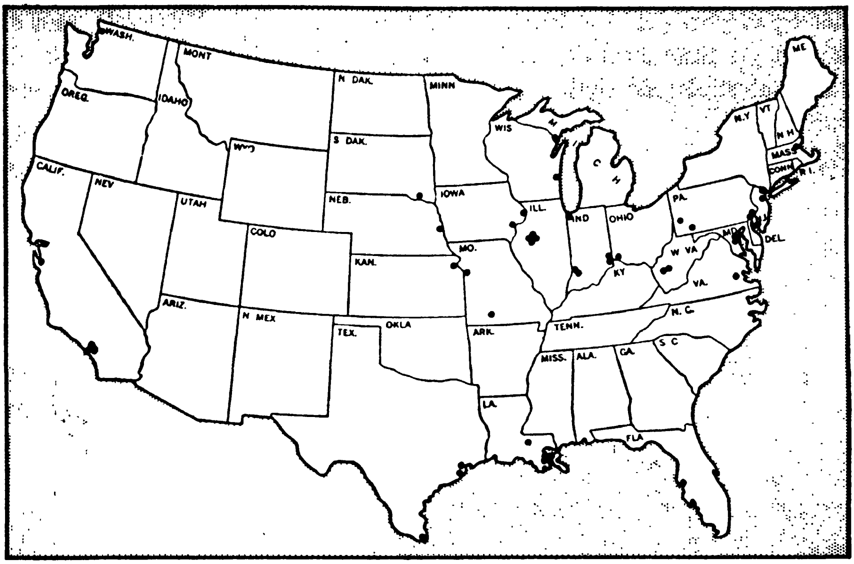
In the over-all picture, many factors must be considered, but important points to be remembered in connection with interprocess economics are that plants must be close to the raw-material supply and yet not too far from the alcohol market; waste-disposal facilities must be adequate;

and in certain cases, minor raw materials such as sweet potatoes, pineapple juice, cactus, and Jerusalem artichokes may be economically feasible.

History is sometimes helpful in predicting future trends, and so the following data on sources of industrial alcohol may be helpful:

1935: molasses—85.5%; grain— 2.7%; synthetic— 9.7%; other— 2.1%
1939: molasses—67.6%; grain— 7.7%; synthetic—23.8%; other— 0.9%
1942: molasses—68.1%; grain— 9.1%; synthetic—21.4%; other— 1.4%
1944: molasses—32.6%; grain—32.4%; synthetic—17.9%; other—17.1%
1948: molasses—38.7%; grain— 9.4%; synthetic—38.2%; other—13.7%

That data since 1939 may not accurately reflect normal conditions is shown by the ceiling prices allowed by the Office of Price Administration



Location of Industrial Alcohol Plants

for a gallon of 190-proof alcohol in 1943: from molasses, 48 cents; grain, 70 cents; synthetic, 24 cents; sulfite, $1.08. In all fairness to sulfite liquor, it must be said that the plant in question (in Canada) had only been operating several months.

The future of the alcohol industry depends largely on trends in synthetic-rubber manufacture and the decision of politicians with respect to alcohol fuels. A majority of technical men do not believe that either outlet will be a large one for alcohol in the near future. Alcohol will then enter its usual channels, in which it competes with many other materials, as in the antifreeze market. Lower costs should enlarge these markets.

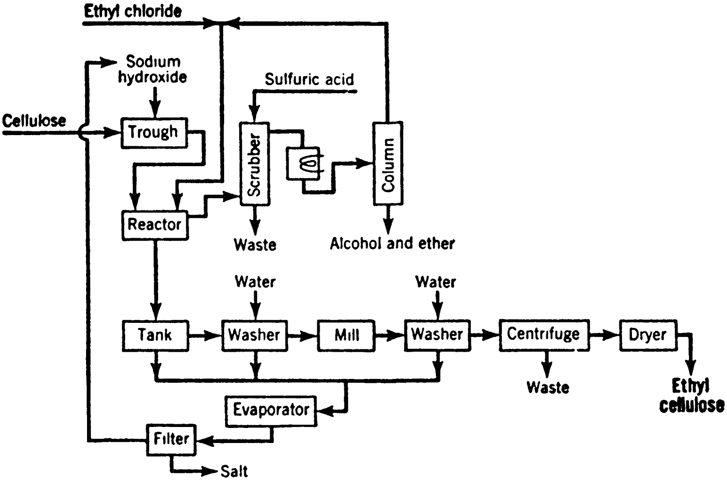
On the other hand, the competition of ethylene glycol and methanol in the antifreeze market and isopropyl alcohol in the general solvent field must not be overlooked. Certainly at present, synthetic alcohol has the lead on other processes, but probable technical advances in the fermentation industry, such as continuous cooking and fermentation, yeast re-use, mold enzyme conversion, and greater utilization of by-products, as well as the possibility of cheaper raw materials, may allow fermentation processes to meet this competition.

A new and uncertain competitive factor in the ethyl alcohol field is the Fischer–Tropsch hydrocarbon synthesis process, which is expected to produce large quantities of industrial alcohol as one of several by-products. It is estimated that such a plant producing 100,000 bbl gasoline per day would produce 120,000,000 gal per yr of alcohol (note that 1947 alcohol production in the United States was only 300,000,000 gal), plus an equivalent amount of other solvents, consisting of practically all the aliphatic alcohols, aldehydes, ketones, and acids containing two to five carbon atoms.

ETHYL CELLULOSE

$[C_6H_7O_2(OC_2H_5)_3]_x$

From Alkali Cellulose and Ethyl Chloride



Reaction

$$\underset{\text{Cellulose}}{[C_6H_{10}O_5]_x} + 3xNaOH \rightarrow [C_6H_7O_2(ONa)_3]_x + 3xH_2O$$

$$[C_6H_7O_2(ONa)_3]_x + 3xC_2H_5Cl \rightarrow [(C_6H_7O_2(OC_2H_5)_3]_x + 3xNaCl$$

85–90% yield

Material Requirements

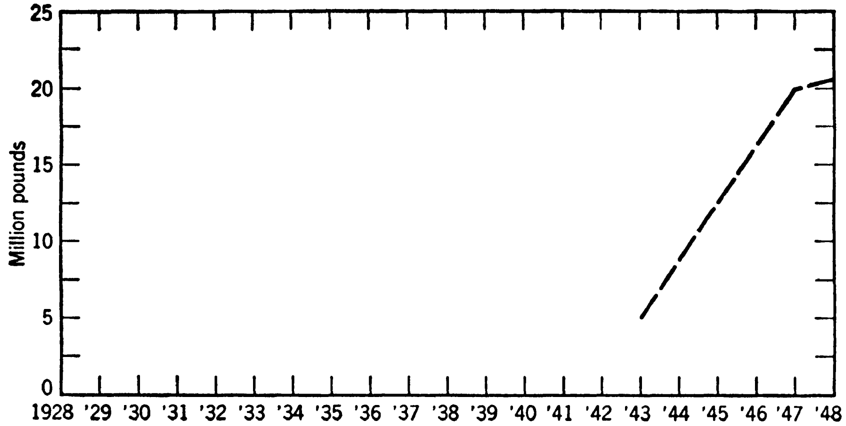
Basis—1 ton ethyl cellulose

Cellulose (purified)	1,600 lb	Sulfuric acid	Small
Sodium hydroxide (50%)	2,400 lb	Ethyl chloride	1,900 lb

Process

A cellulosic material such as cotton linters or sulfite pulp is treated with a concentrated solution of sodium hydroxide. The alkali cellulose ormed is then alkylated with ethyl chloride to yield ethyl cellulose.

Raw cotton linters are purified by treatment with sodium hydroxide to solubilize the hulls, oils, and waxes. The mass, after washing, is bleached with chlorine, rewashed, and sheeted. The purified cotton linters or wood pulp are shredded and charged into a covered horizontal trough known as a "wetter." Here the cellulose is moistened by a spray of concentrated sodium hydroxide solution. The wetted material is moved through the Monel trough by a screw conveyer to the reactors. It is charged batchwise into high-pressure (700-psi) steam-jacketed, nickel-lined autoclaves along with ethyl chloride. The amount of ethyl chloride charged is dependent for the most part on the degree of etherification desired. The usual commercial product contains 2.4 to 2.5 ethoxy groups per glucoside unit of the cellulose chain.



Production—Ethyl Cellulose (Estimated)

After the reactor is charged, the temperature is raised to about 200°C. The alkali cellulose and excess sodium hydroxide react with ethyl chloride, forming ethyl cellulose, ether, alcohol, and sodium chloride. At the end of the reaction cycle, the ethyl alcohol, ether, and unreacted chloride are flashed off through a lead-lined scrubber. After being scrubbed with dilute sulfuric acid to remove low-boiling contaminants, the solvents are condensed and stored. Later these solvents are fractionated to recover the unreacted ethyl chloride for re-use and the ether and alcohol for ethyl chloride production (see *Ethyl Chloride*).

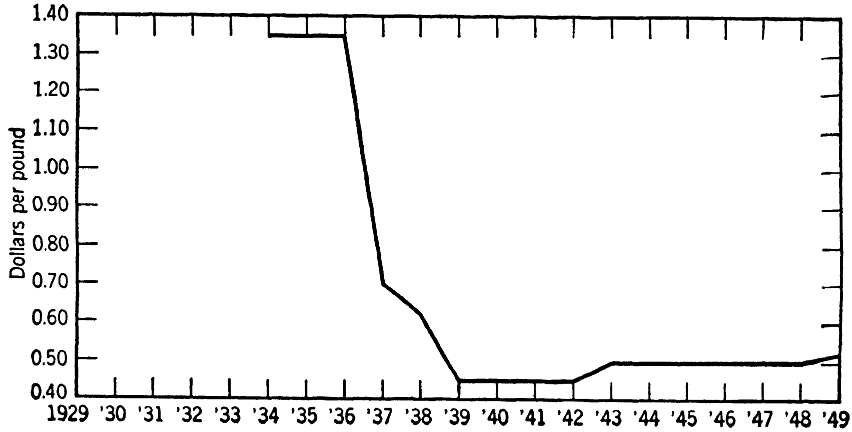
During the solvent evaporation from the reactor, the ethyl cellulose precipitates from the solution of sodium hydroxide and sodium chloride. The slurry is discharged into a tank where the caustic liquor is drained off. The large granules of ethyl cellulose are washed with water to remove adhering salt and are dropped into hammer or knife-cutter mills.

After grinding, the powder is rewashed with water to remove trapped caustic and salt. The resulting wash liquor is combined with the previous caustic liquor. The weak caustic solution is then charged into double-effect evaporators, where the salt is thrown out of solution and the caustic is brought up to 50 per cent strength for re-use.

The water slurry of ethyl cellulose, after a purification treatment, is centrifuged to reduce the water content to about 50 per cent. The material is discharged into a dryer, where the moisture is reduced to 0.5 per cent, and then packaged. Approximately 125 lb ethyl cellulose is produced per 100 lb cellulose charged.

Use Pattern

	Per cent
Plastics	70
Protective coatings	30
	100



Price—Ethyl Cellulose

Miscellaneous

Properties. Fine, white granules. Standard grade of 47 to 48 per cent ethoxyl content. Soluble and compatible with a wide variety of solvents, resins, waxes, oils, and plasticizers.

Specific gravity	1.07–1.18
Grams per cubic inch	18.7
Odor	Slight to none
Refractive index, n_D	1.47
Color range	Extensive

Stability

Water absorption (after immersion 24 hr)		1.2-2.5 per cent
Effect of age:	Outdoor resistance	Good
	Indoor resistance	Excellent
	Sunlight resistance	Good

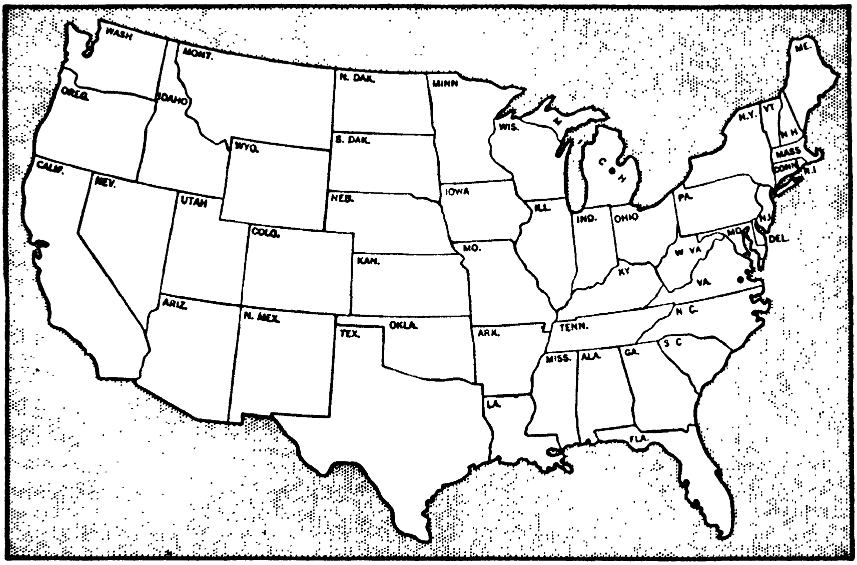
Not affected by alkalies; reacts slightly to weak acids; decomposed by strong acids; very soluble in many organic solvents.

Grades. Standard (47 to 48 per cent ethoxyl content).

Containers and Regulations. Bags and fiber drums.

Economic Aspects

Ethyl cellulose is a newcomer to the field of cellulose derivatives, still dominated by cellulose acetate and cellulose nitrate. Like the latter material, the trisubstituted product is of little value. Accordingly, various types of ethyl cellulose are on the market, ranging in substitution value from 2.15 to 2.60 ethoxy groups per glucose unit, or 43 to 50 per cent ethoxyl content.



Location of Ethyl Cellulose Plants

The distinguishing feature of ethyl cellulose is its versatility, of which one factor is a wide solubility and compatability with other materials. A disadvantage is its susceptibility to oxidation when improperly compounded. As more becomes known concerning its limitations and capabilities, wider use may be expected. Attempts to put ethyl cellulose in the fiber field have been unsuccessful so far, but its chemical properties and excellent dyeing properties make it look promising.

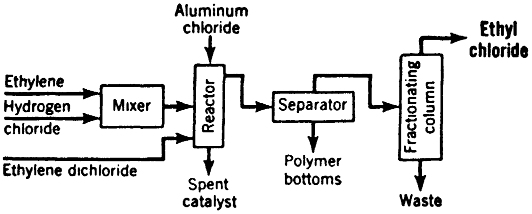
It must compete, however, in the future with other cellulose ethers, many types of which are appearing on the market in experimental quantities.

The minimum economic size of plant is about 2,000,000 lb capacity per yr. A complete plant of this size costs about $1,000,000.

ETHYL CHLORIDE

C_2H_5Cl

From Ethylene and Hydrogen Chloride



Reaction

$$C_2H_4 + HCl \xrightarrow{AlCl_3} C_2H_5Cl$$

90% yield

Material Requirements

Basis—1 ton ethyl chloride

Ethylene	975 lb
Hydrogen chloride	1,250 lb
Aluminum chloride	Small

Process

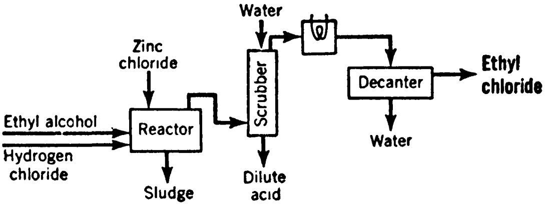
Ethyl chloride is produced by addition of hydrogen chloride to ethylene under anhydrous conditions in the presence of a catalyst such as aluminum chloride.

Ethylene gas and substantially anhydrous hydrogen chloride are mixed in approximately equimolecular proportions and passed into a reactor partially filled with ethylene dichloride or a mixture of ethyl chloride and ethylene dichloride. In the presence of aluminum chloride, at a temperature of 35 to 40°C, the exothermic hydrochlorination takes place. The vaporized products are fed into a column or "flash drum," where the lower-boiling ethyl chloride is separated from the heavier polymers. The crude ethyl chloride is refined by fractionation. Catalyst is continually withdrawn, and new make-up catalyst is added.

At temperatures above 300°C in the presence of iron or cuprous chloride, ethane and chlorine react to yield ethyl chloride. This process may be attractive, because it can utilize waste gases.

Equimolecular mixtures of ethane and methane may also be photochemically chlorinated to yield a product containing 85 per cent ethyl chloride and 15 per cent ethylene dichloride. A chlorine–ethane ratio of approximately unity, a residence time of 1.0 to 1.5 sec, and a temperature between 100 and 200°C give best results (75 per cent yield of ethyl chloride based on ethane). The reaction products must be cooled very quickly to obtain maximum yield.

From Ethyl Alcohol and Hydrogen Chloride



Reaction

$$C_2H_5OH + HCl \rightarrow C_2H_5Cl + H_2O$$

95–98% yield

Material Requirements

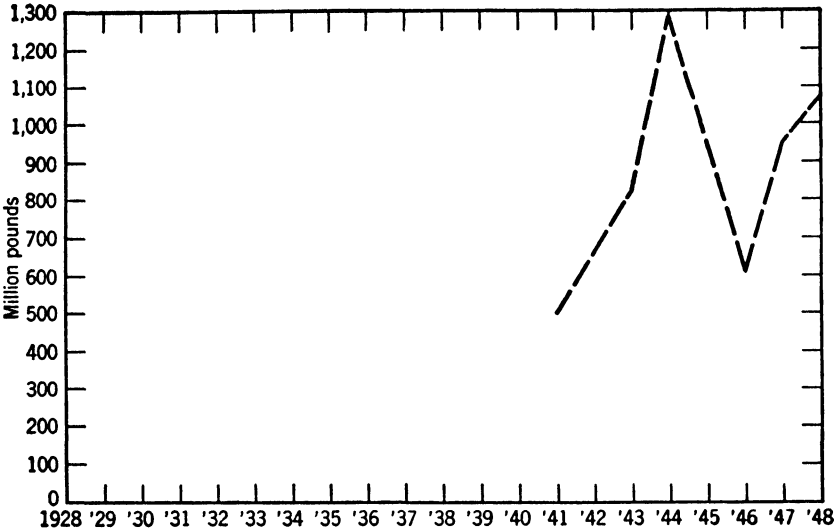
Basis—1 ton ethyl chloride (99%)

Ethyl alcohol	1,500 lb
Hydrogen chloride	1,200 lb
Catalyst loss	Small

Process

The reaction of ethyl alcohol and hydrogen chloride in the presence of a catalyst yields ethyl chloride.

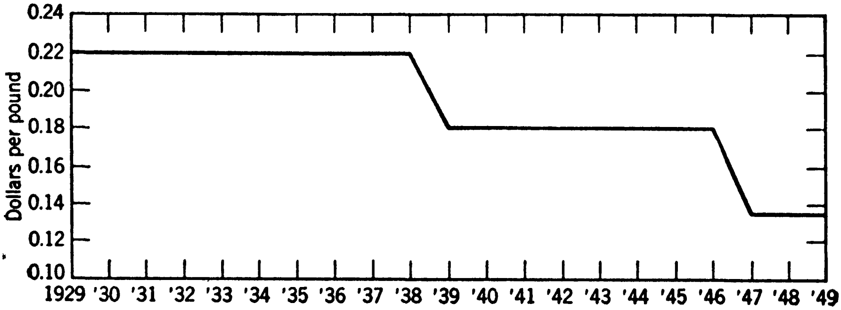
Warm 95 per cent ethyl alcohol is fed into the bottom of a jacketed glass-lined reactor containing a 45 per cent aqueous zinc chloride solution. Countercurrent to the alcohol, substantially anhydrous hydrogen chloride is fed into the aqueous zinc chloride solution, which is maintained at about 145°C. The rates of feed are approximately 0.17 and 0.13 parts per hour per part of zinc chloride solution for the alcohol and hydrogen chloride, respectively. The reactor pressure is maintained at 30 psi. The catalyst concentration remains about constant, while vapors of ethyl chloride, water, and some hydrogen chloride are withdrawn from the reactor and passed countercurrent to a stream of water at 80°C in a glass-lined scrubber. The scrubber, operating at about 30 psi, removes the free acid from the incoming vapors. The scrubbed vapors are cooled to about 20°C; at the condenser pressure (30 psi) substantially complete condensation takes place. The liquid is passed into a decanter where ethyl chloride is separated from water. The process operates continuously to produce 99 per cent ethyl chloride in a yield of 95 to 98 per cent based on ethyl alcohol.



Production—Chlorinated Ethanes and Ethylenes (Estimated. No data available on ethyl chloride alone until 1948—274,660,000 lb)

Use Pattern

Tetraethyl lead Ethyl cellulose Refrigerant Anesthetic	No breakdown available



Price—Ethyl Chloride

Miscellaneous

Properties. Colorless gas at ordinary temperatures. Easily compressed to a colorless, highly flammable, volatile liquid possessing an ether-like odor.

Mol. wt.	64.52	M.P.	−138.3°C
Sp. gr.	0.917 6°C/6	B.P.	12.27°C

Vapor pressure 1,000 mm at 20°C

Soluble in alcohol, ether, and most hydrocarbon solvents. Slightly soluble in water (0.45 per cent at room temperature).

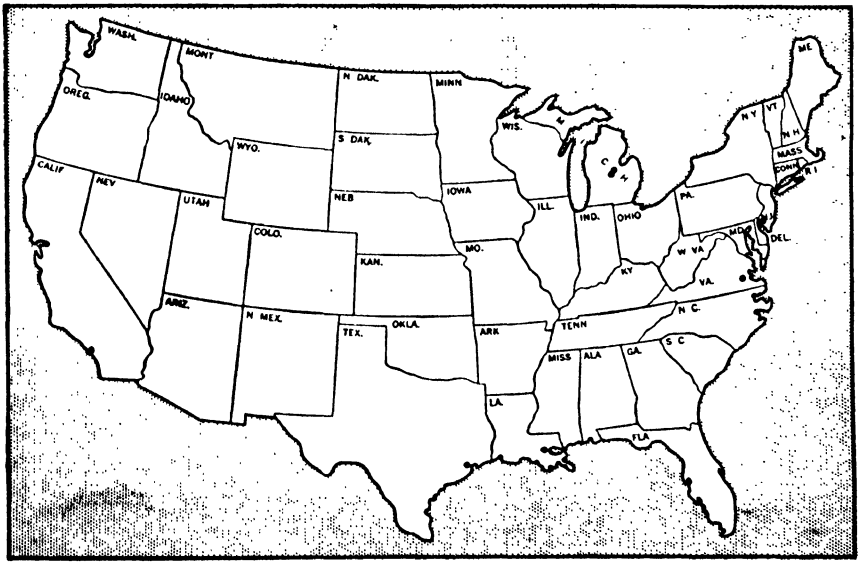
Flash point (closed cup)	−58°F
Ignition temperature	966°F
Vapor density (air = 1)	2.22
Explosive limits (% by volume in air)	Lower 3.6– 4.3 Upper 11.2–15

Grades. Technical, and USP.

Containers and Regulations. Tank cars, cylinders, and hermetically sealed tubes. Stable and noncorrosive when dry, but readily hydrolyses in the presence of water or alkalies. Red ICC shipping label required.

Economic Aspects

The major use for ethyl chloride is in the manufacture of tetraethyl lead, and, accordingly, production is governed by demand for the anti-



Location of Ethyl Chloride Plants

knock material. There are, of course, no competitive materials for ethyl chloride either for this use or in the manufacture of ethyl cellulose. As a refrigerant, it meets competition from other chlorinated hydrocarbons, such as methyl chloride and dichlorodifluoromethane. Its use as a solvent is greatly limited by its high vapor pressure. In anesthetics a variety of competitive materials exist. For use as a refrigerant or solvent, both price and suitability to particular systems are controlling factors in the choice of competing products.

Most ethyl chloride is made by the addition of hydrogen chloride to ethylene, which process is replacing the older one using ethyl alcohol as a starting material. One new plant makes ethyl chloride by the controlled chlorination of ethane. Fundamentally, this should be the cheapest of all three processes, if an adequate market can be found for the polychlorinated by-products.

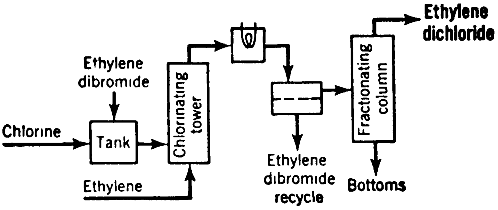
Plants may be expected to be of the same size and cost as ethylene dichloride plants (see *Ethylene Dichloride*).

ETHYLENE DICHLORIDE

(1,2-DICHLOROETHANE)

$ClCH_2CH_2Cl$

From Ethylene and Chlorine



Reaction

$$CH_2{=}CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl$$

90% yield

Material Requirements

Basis—1 ton ethylene dichloride

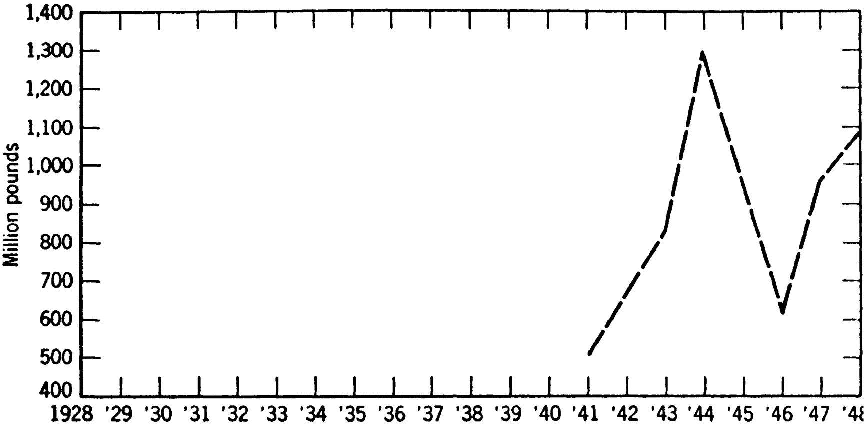
Ethylene	630 lb
Chlorine	1,600 lb
Ethylene dibromide	Small

Process

Ethylene dichloride is produced by the vapor or liquid-phase reaction of ethylene and chlorine in the presence of a catalyst.

Chlorine gas is bubbled through a tank of ethylene dibromide, and the mixed vapors are passed into a chlorinating tower maintained at 40 to 50°C. The chlorine meets a stream of ethylene gas, and the resulting reaction products are passed from the top of the tower through a partial condenser (above 85°C) into a separator. The ethylene dibromide liquefies and is returned to the process. Gaseous ethylene dichloride is fed into a fractionating column to yield a refined product. The yield is about 90 per cent.

Many alternative procedures are known and vary mainly in the catalyst used and conditions of reaction. One process uses a feed of gaseous chlorine and ethylene. A catalyst of aluminum or ferric chloride is utilized in a tubelike reactor. Operating at an intake temperature of 15°C, exhaust temperature above 135°C, and essentially atmospheric pressure, the reaction yields gaseous products which are separated by cooling to −5°C. The separated dichloride is refined in the manner described previously.

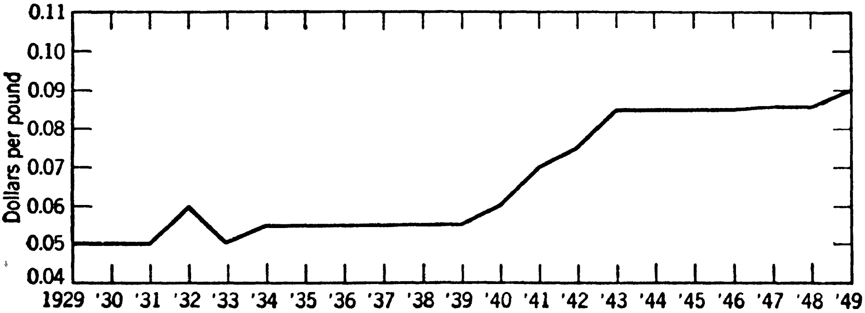


Production—Chlorinated Ethanes and Ethylenes (Estimated. No data available on ethylene dichloride alone until 1948—235,893,000 lb)

Use Pattern

Thiokol manufacture
Antiknock fluids
Ethylenediamine
Solvent
Insecticide

No breakdown available



Price—Ethylene Dichloride

Miscellaneous

Properties. Colorless, oily liquid with a pleasant chloroform-like odor and a sweet taste.

Mol. wt.	98.97	M.P.	−35.3°C
Sp. gr.	1.257 20°C/4	B.P.	83.7°C

Weight per gallon	10.5 lb (20°C)

Soluble in alcohol, chloroform, ether, and most common solvents. Very slightly soluble in water (0.9 per cent at 0 and 30°C).

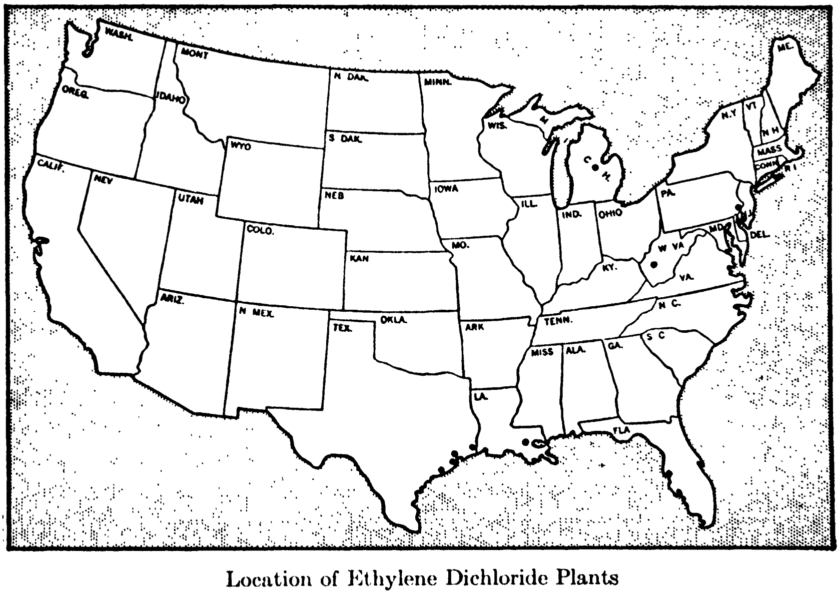
Flash point (closed cup)	56°F
Ignition temperature	775°F
Vapor density (air = 1)	3.42
Explosive limits (% by volume in air)	Lower 6.2 Upper 15.9

Grades. Technical.

Containers and Regulations. Tank cars, drums, cans, and bottles. Stable in presence of water, alkalies, and acids, and resistant to oxidation. Noncorrosive to metals. Red ICC shipping label required.

Economic Aspects

Ethylene dichloride is usually manufactured by concerns making a variety of chlorinated hydrocarbons or recovered as a by-product. Most of the by-product material is obtained in the manufacture of ethylene



Location of Ethylene Dichloride Plants

chlorohydrin and allyl chloride. The former product, once an important intermediate in the manufacture of ethylene glycol, is being replaced by ethylene oxide (see *Ethylene Glycol*), and so this by-product source of ethylene dichloride is becoming much less important. Undoubtedly, some ethylene dichloride is also recovered from the direct chlorination of ethane to ethyl chloride (see *Ethyl Chloride*).

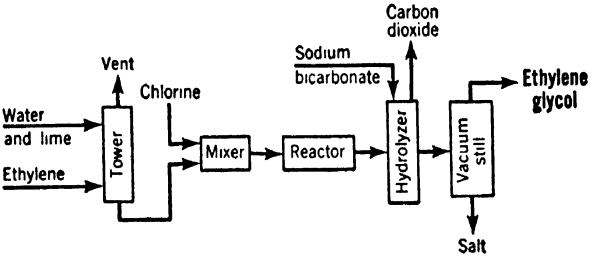
For solvent purposes, ethylene dichloride meets keen competition from other chlorinated hydrocarbons, but in its uses in the synthesis of Thiokol and ethylenediamine it has no important competitive materials. In the soil-fumigant field, D–D mixture (a mixture of 1,3-dichloropropylene and 1,2-dichloropropane; see *Allyl Alcohol*) offers very serious competition.

Ethylene dichloride plants are fairly large, ranging in capacity from 20,000,000 to 100,000,000 lb per yr. Such plants may be expected to require an investment of $200 to $300 per annual ton capacity, depending on plant size.

ETHYLENE GLYCOL

$HOCH_2CH_2OH$

From Ethylene through Ethylene Chlorohydrin



Reaction

$$CH_2{=}CH_2 + HOCl \rightarrow CH_2OHCH_2Cl$$

$$CH_2OHCH_2Cl + NaHCO_3 + H_2O \rightarrow$$

$$CH_2OHCH_2OH + CO_2 + H_2O + NaCl$$

65–70% yield

Material and Utility Requirements*

Basis—1 ton ethylene glycol

Ethylene	1 ton	Sodium hydroxide	80 lb
Chlorine	2.35 tons	Steam	24,000 lb
Milk of lime (100% CaO)	2.2 tons	Electricity	160 kw-hr
		Water	80,000 gal

Process

The reaction between ethylene and hypochlorous acid yields ethylene chlorohydrin, which may be converted either directly to ethylene glycol by hydrolysis or to ethylene oxide by reaction with alkali and then to the glycol by hydrolysis.

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* Indirect process (no $NaHCO_3$).

To produce ethylene chlorohydrin by a continuous process, ethylene is passed under a pressure of 200 atm at 20°C into a tower. A solution of hydrated lime is then charged into the tower, so that under the stated temperature and pressure about 28 g of ethylene per liter of alkali results. The solution is pumped under pressure into a mixer, where it meets a stream of chlorine at the rate of 1 mole chlorine per liter of alkali solution. The chlorine reacts with the hydrated lime to form calcium oxychloride, which is immediately decomposed to form hypochlorous acid and calcium chloride, according to the following equations:

$$CaO + Cl_2 \rightarrow CaClOCl$$

$$CaClOCl + Cl_2 + H_2O \rightarrow CaCl_2 + 2HOCl$$

The hypochlorous acid reacts with the ethylene in solution to give ethylene chlorohydrin. The reaction takes place at essentially room temperature and at about 200 atm pressure.

The ethylene chlorohydrin–calcium chloride solution (35 to 40 per cent chlorohydrin) is withdrawn from the reactor for treatment in one of two ways.

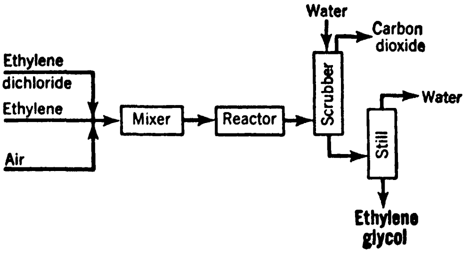
The first method employs direct hydrolysis. The solution is treated with the theoretical amount of sodium bicarbonate solution at 70 to 80°C in a closed steam-jacketed kettle fitted with an efficient agitator. Carbon dioxide is evolved and may be used to carbonate fresh caustic solution. After 4 to 6 hr the evolution of carbon dioxide ends, and the crude glycol solution is passed into a vacuum still. Here, under reduced pressure, the solution is concentrated and separated from the salt by distillation.

Because the high-boiling glycol is separated with difficulty from the salt, the second method of indirect hydrolysis is often preferred from an engineering standpoint.

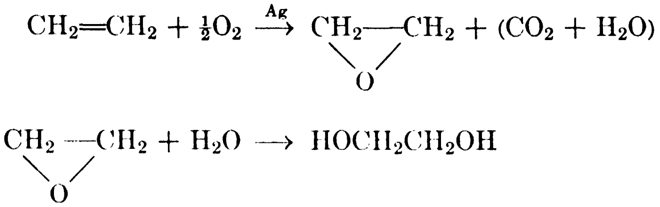
The ethylene chlorohydrin solution is heated with lime or sodium hydroxide to yield ethylene oxide. The oxide is easily distilled from the salts and is then hydrated with slightly acidified water under high-temperature and pressure conditions. The crude glycol mixture is concentrated in evaporators and then fed to a still to separate the three glycols into mono-, di-, and triethylene glycols.

The major by-products formed in the chlorination and dehydrochlorination steps are ethylene dichloride and dichloroethyl ether.

From Ethylene and Oxygen



Reaction



$$CH_2{=}CH_2 + \tfrac{1}{2}O_2 \xrightarrow{Ag} \underset{\diagdown\,O\,\diagup}{CH_2{-}CH_2} + (CO_2 + H_2O)$$

$$\underset{\diagdown\,O\,\diagup}{CH_2{-}CH_2} + H_2O \longrightarrow HOCH_2CH_2OH$$

50% yield

Material Requirements

Basis—1 ton ethylene glycol

Ethylene	1,800 lb
Air	19,000 lb
Ethylene dichloride	36 lb
Silver (catalyst replacement)	1 lb

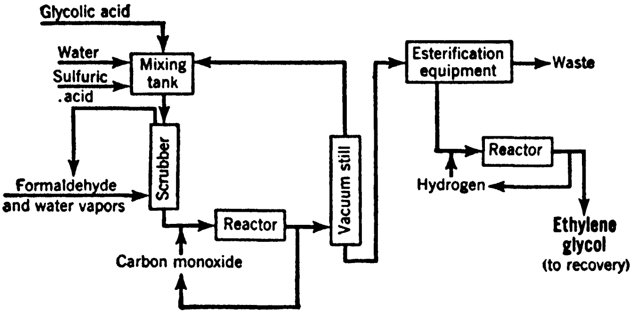
Process

The catalytic oxidation of ethylene with air yields ethylene oxide and carbon dioxide. Ethylene oxide may then be hydrated to yield ethylene glycol.

Ethylene and air are mixed in a volume ratio of about 1 to 10 and passed over a catalyst composed of silver oxide supported on corundum. Generally, an anticatalyst such as ethylene dichloride (about 2 per cent based on the weight of ethylene) is added to the ethylene feed to suppress the formation of carbon dioxide. At essentially atmospheric pressure and temperatures of 270 to 290°C, when a contact time of about 1 sec is used, 60 to 70 per cent of the ethylene is converted to ethylene oxide.

The reaction products are led into a scrubber where under pressure the ethylene oxide is absorbed and hydrated to ethylene glycol while carbon dioxide is either vented or recovered. Ethylene glycol is obtained in yields of about 70 per cent.

From Formaldehyde and Carbon Monoxide



Reaction

$$CH_2O + CO + H_2O \rightarrow CH_2OHCOOH$$

$$CH_2OHCOOH + ROH \rightarrow CH_2OHCOOR + H_2O$$

$$CH_2OHCOOR + 2H_2 \rightarrow CH_2OHCH_2OH + ROH$$

75% yield

Material Requirements

Basis—1 ton ethylene glycol

Formaldehyde	1,300 lb	Hydrogen	150 lb
Carbon monoxide	1,250 lb	Sulfuric acid	90 lb

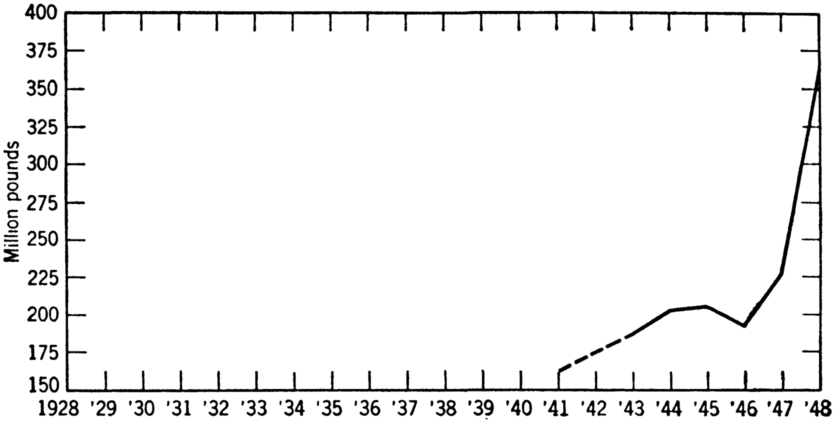
Process

Ethylene glycol may be manufactured by hydrogenation of an ester of glycolic acid. The acid is produced by the interaction of formaldehyde, water, and carbon monoxide at superatmospheric pressure.

Vapors consisting of one part formaldehyde and one part water, such as are obtained by the catalytic oxidation of methanol, are passed into the bottom of a scrubbing column. Here they contact a solvent mixture consisting, on a molal basis, of 2 parts of glycolic acid, 1 part of water, and approximately 0.02 part of sulfuric acid. The resulting solution leaving the bottom of the column (2 parts glycolic acid, 1 part formaldehyde, 2 parts water, and 0.02 part sulfuric acid) is passed through a continuous reactor in the presence of excess carbon monoxide at 200°C and 700 atm. Time of contact is less than 5 min.

The formaldehyde and carbon monoxide react to produce an effluent containing essentially 3 parts glycolic acid, 1 part water, and 0.02 part sulfuric acid. This mixture is distilled under 80 to 100 mm Hg pressure at such conditions that glycolic acid is removed from the bottom of the column; the overhead vapors (2 parts glycolic acid and 1 part water) are returned to the scrubber to absorb more formaldehyde and water. The yield of glycolic acid ranges from 90 to 95 per cent based on formaldehyde.

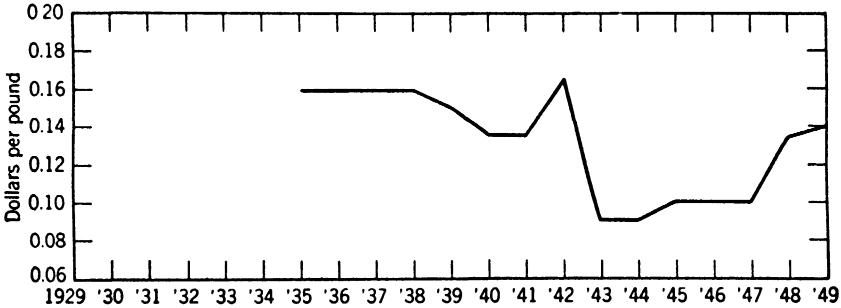
The glycolic acid leaving the bottom of the column may be purified by esterification and subsequent distillation. The resulting ester (3 parts) is reacted with hydrogen (97 parts) in the presence of a chromite catalyst. The hydrogenation is carried out at approximately 200°C, 30 atm pressure, and a space velocity of 20,000 reciprocal hours. Ethylene glycol is formed in 90 to 95 per cent yield.



Production—Ethylene Glycol

Use Pattern

	1948 (est.), per cent
Antifreeze	65
Dynamite	5
Cellophane	5
Miscellaneous and export	25
	100



Price—Ethylene Glycol

Miscellaneous

Properties. Colorless, sirupy hygroscopic liquid with a sweet taste.

Mol. wt.	62.07	M.P.	−15.6°C
Sp. gr.	1.116 20°C/20	B.P.	197.2°C
Weight per gallon	9.28 lb (20°C)		

Soluble in water, alcohol, and ether. Lowers the freezing point of water.

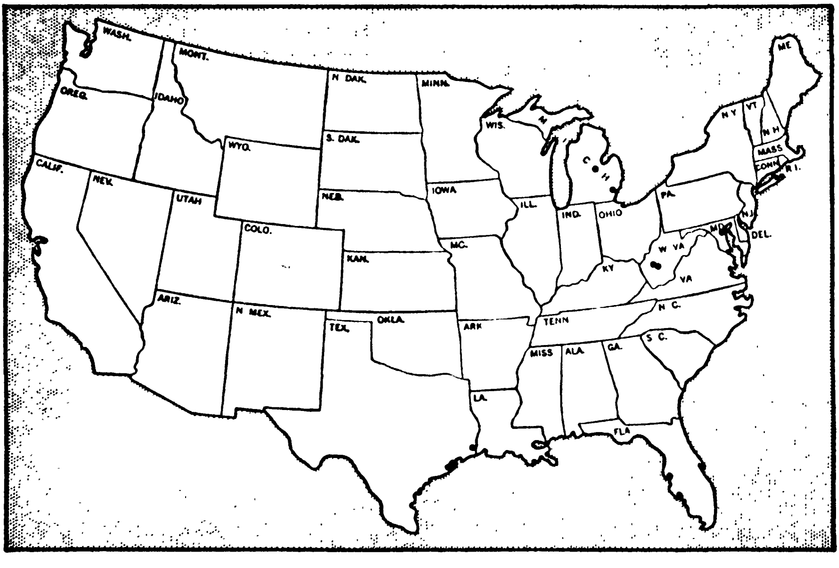
Flash point (closed cup)	232°F
Ignition temperature	775°F
Vapor density (air = 1)	2.14
Explosive limits (% by volume in air)	Lower 3.2

Grades. Technical.

Containers and Regulations. Tank cars, drums, cans, and bottles. No ICC shipping label required.

Economic Aspects

The various processes for manufacturing ethylene glycol appear to be competitive and depend to a great extent economically on other products made by the manufacturer. From an operating standpoint, manufacture from the intermediate, ethylene oxide, is simpler than direct manufacture from ethylene chlorohydrin, the original process used. On



Location of Ethylene Glycol Plants

the other hand, a plant to manufacture ethylene oxide directly by oxidation probably costs 50 per cent more than does a plant utilizing the indirect process.

In its chief use, that of a coolant and permanent "antifreeze" material, ethylene glycol must compete against glycerine, ethyl alcohol, isopropyl alcohol, and methanol. Ethylene glycol has a strong position in this field, and indications are that it will gain even a stronger position in the future. Recent chemical outlets, which may become quite large, are in the manufacture of glyoxal by catalytic oxidation and in the manufacture of a textile fiber by esterification with terephthalic acid.

The various glycol manufacturing processes are well protected by patents, and no information is available on economic plant size and investment. Most actual plants are estimated to have capacities between 10,000,000 and 50,000,000 lb per yr. Cheap ethylene or water gas is required for economic production.

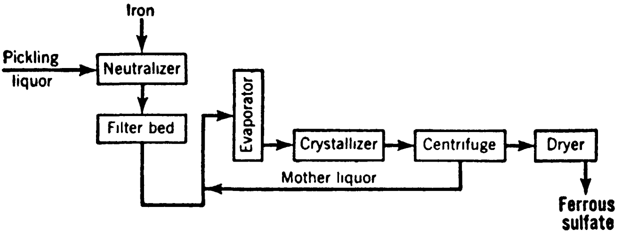
Two new producers have recently entered the ethylene glycol field, one with a plant at Port Neches, Texas (using ethylene oxide as an intermediate), and another with a plant at Wyandotte, Mich. (processing a mixture of ethylene and propylene through the chlorohydrin stage).

FERROUS SULFATE

(COPPERAS)

$FeSO_4 \cdot 7H_2O$

From Steel Pickling Liquor



Reaction

$$\underset{\text{Waste pickle liquor}}{FeSO_4 + H_2SO_4} + nH_2O + Fe \rightarrow 2FeSO_4 \cdot 7H_2O + H_2 + (n - 14)H_2O$$

Material Requirements

Basis—1 ton ferrous sulfate heptahydrate

Pickling liquor (28°Bé)	5,000 lb
Scrap iron	150 lb

Process

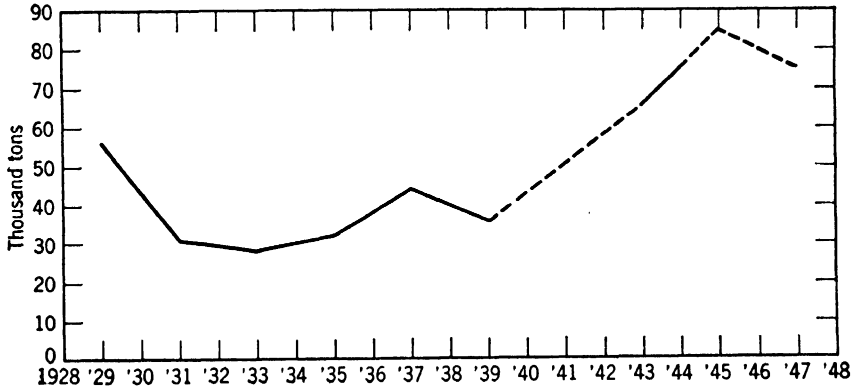
Ferrous sulfate is formed by the action of sulfuric acid on iron. The steel-pickling processes, in which steel surfaces are cleaned preparatory to tinning, galvanizing, electroplating, or enameling, produce a waste liquor containing, on the average, 15 per cent ferrous sulfate. This waste liquor serves as the raw material for most ferrous sulfate production.

The steel-mill pickling liquors vary widely in specific gravity and free acid and must be treated accordingly. Generally, the gravity varies from 17 to 33°Bé and the free acid from 2 to 7 per cent. The liquor is run into acid-proof neutralizing tanks, where scrap iron is added to reduce the free acid content to about 0.03 per cent. After neutralization (from 12 to 60 hr), the liquor is filtered through a bed of sand or coke and run to concentrators. Triple-effect vacuum evaporators (constructed of extra-heavy castings with copper tubes) may be used. The concentrated liquor (about 42°Bé) is run to batch or continuous crystallizers.

An alternate procedure for concentrating the waste liquor is to charge the dilute liquor (about 28°Bé) into a lead-lined reaction vessel. Enough scrap iron and sulfuric acid are added at 180°F to raise the concentration to 42°Bé. The solution is allowed to settle and after filtration is run to crystallizers.

The hot (160°F) concentrated liquor from the evaporator (or settling tank) is allowed to cool to room temperature in the crystallizers; crystals ($FeSO_4 \cdot 7H_2O$) deposit until the gravity has fallen to about 26°Bé. Without artificial cooling, the crystallization takes 2 to 3 days. The crystals are filtered and washed (with warm water) in a centrifuge. The mother liquors are returned to either the neutralizing tank or the evaporator.

The crystals may be broken and screened and are then dried with warm air (about 140°F) in rotary drum dryers. Overheating must be avoided, since the ferrous sulfate with 7 molecules of water easily loses 2 molecules to form ferrous sulfate pentahydrate ($FeSO_4 \cdot 5H_2O$), which is known as siderotilate. Further drying produces ferrous sulfate monohydrate (approximately $FeSO_4 \cdot 1\frac{1}{2}H_2O$). The main difficulty in the process is the prevention of oxidation by air, whereby ferrous sulfate is changed to ferric sulfate. This is generally avoided by maintaining a slight excess of sulfuric acid. During the heating and settling operations, small quantities of iron may be added to the liquor to provide a slight reaction (reducing) with the free sulfuric acid, thereby counteracting surface oxidation.

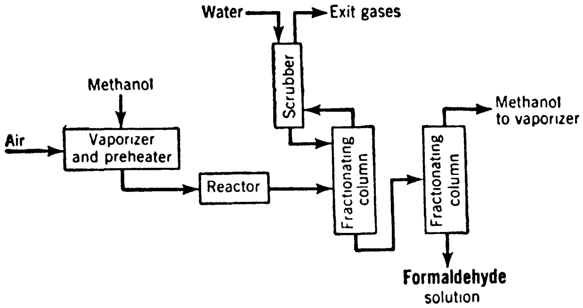


Production—Ferrous Sulfate (Production for sale—1929–39; total production 1943–44 and 1947)

FORMALDEHYDE

HCHO

From Methanol



Reaction

$$CH_3OH + \tfrac{1}{2}O_2 \text{ (air)} \xrightarrow{\text{Catalyst}} CH_2O + H_2O$$

$$CH_3OH \longrightarrow CH_2O + H_2$$

85–90% yield

Material Requirements

Basis—1 ton formaldehyde (37%)

Methanol	930 lb	62 ft^3.
Air	25,000 cu ft at 32°F	

Process

Air and methanol are mixed in such a ratio that the gas mixture contains 30 to 50 per cent methanol by volume. This is generally accomplished by mechanical mixing or by maintaining the methanol at a constant level and temperature in the vaporizer, through which air is either drawn by vacuum or forced by compression. The alcohol–air mixture passes through a preheater (100 to 300°C), in order to remove any residual alcohol spray and to eliminate the possibility of partial condensation, and then to the reactor.

The catalyst chamber (reactor) contains a metal or metal oxide catalyst. Silver and copper are the most satisfactory metal catalysts and are generally used in the form of multilayer gauze or screens. The reaction over these catalysts is essentially a combination of dehydrogenation and oxidation, the former being responsible for high yields whereas the latter supplies heat and aids in keeping the catalyst active. Therefore, an optimum balance between the two reactions is maintained by using a sufficient amount of air to make the net reaction thermally self-supporting once it has been initiated. The catalyst temperature approximates 450 to 600°C, and the contact time is about 0.01 sec.

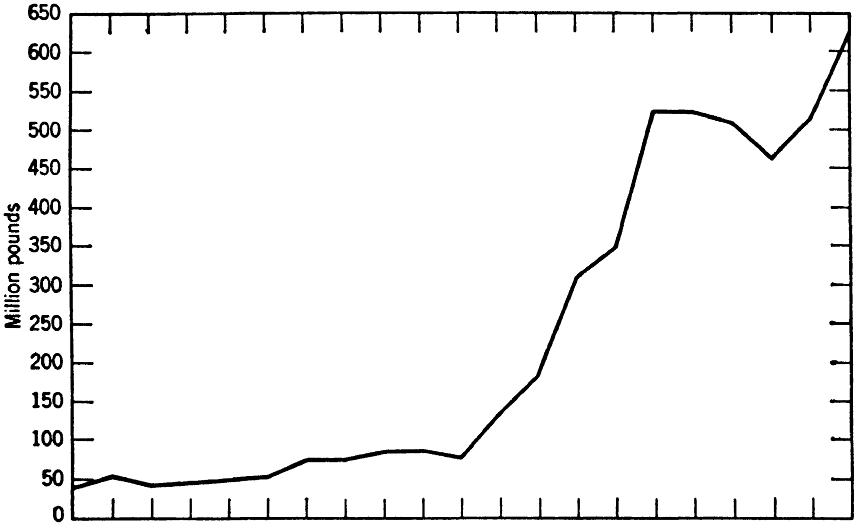
The most satisfactory metal oxide catalyst consists of a mixture of the oxides of molybdenum, iron, or vanadium. The reaction over this type of catalyst is mainly one of oxidation and requires a large excess of air (5 to 10 times that required by the metallic catalyst). A very high conversion is obtained by this process, so that very little methanol remains to be removed in subsequent operations.

The hot reaction gases from the converter containing the metal catalyst are delivered directly to a column where a preliminary separation of formaldehyde and unchanged methanol takes place. This is accomplished by multitubular coolers, which are so fixed that alternate scrubbing and cooling is conducted; the gases then pass to a final scrubber fed with cold water and are finally vented to the atmosphere. These exit gases contain 19 to 22 per cent hydrogen and 74 to 75 per cent nitrogen. The hydrogen content is a good indication of the catalyst efficiency, and an analysis of the exit gases for hydrogen may be used for process control. The gases also contain between 4 and 5 per cent carbon dioxide, together with traces of carbon monoxide, oxygen, and methane, which represent direct loss of methanol by over-oxidation.

The combined condensate and scrubber liquor from the main column (containing formaldehyde, water, and approximately 15 per cent unreacted methanol) are fed at suitable points into a fractionating column, where 37 per cent formaldehyde plus the desired amount of methanol stabilizer is removed from the bottom and excess methanol is removed from the top and returned to the vaporizer. Over-all (net) yields of 85 to 90 per cent by weight based on the methanol charged are obtained by using either the metal or metallic oxide catalyst.

From Natural Gas

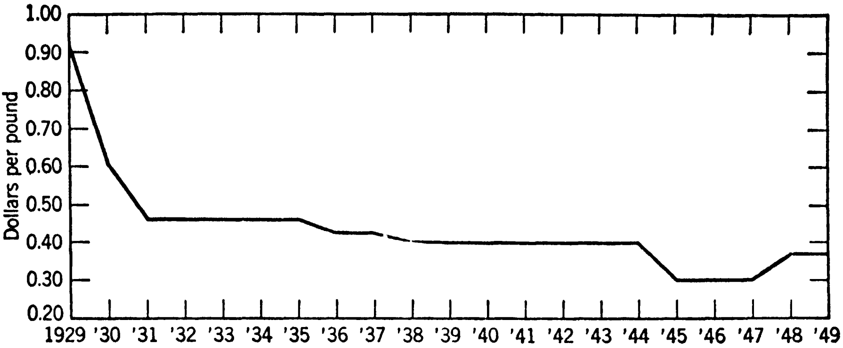
Formaldehyde is also manufactured dir[illegible]m natural gas, methane, and other aliphatic hydrocarbons. This process yields a mixture of products varying with the nature of the starting material. The formaldehyde is generally obtained in the form of dilute solutions from which it must be concentrated. Difficulties are also encountered in the separation of formaldehyde from other aldehydes and by-products formed in the reaction. One such process, which utilizes butane as the starting material, is described under *Acetaldehyde.* A comparable process, using natural gas as the raw material, operates at temperatures of 430 to 480°C and pressures of 7 to 20 atm. Mixed catalysts of aluminum phosphate and metal oxides may be employed. The liquid reaction product contains approximately 34 to 36 per cent methanol, 20 to 23 per cent formaldehyde, and 5 to 6 per cent acetaldehyde, plus varying amounts of higher aldehydes, ketones, alcohols, and water. After preliminary separation, the formaldehyde solution is freed of formic acid by ion-exchange refining.



Production—Formaldehyde (37%)

Use Pattern

	1947 (est.), per cent
Resins	60
Hexamethylenetetramine	4
Pentaerythritol	12
Ethylene glycol	4
Other chemicals	12
Miscellaneous	8
	100



Price—Formaldehyde (37%)

Miscellaneous

Properties. Formaldehyde (100 per cent) is a colorless, pungent, and highly irritating gas, which may be liquefied and solidified by chilling. However, both gas and liquid readily polymerize at ordinary and low temperatures and can be maintained in the monomeric state for only a limited time. Because of this, formaldehyde is not commercially available in the gaseous monomeric form; it is, however, available in both the dissolved and polymerized state. The main properties of formaldehyde solutions and polymers, as well as properties of gaseous monomeric formaldehyde, follow:

Formaldehyde Gas (100 per cent), HCHO.

Mol. wt.	30.03	M.P.	−118°C
Sp. gr.	0.815 (−20°C)	B.P.	−19°C

Soluble in water and polar solvents such as alcohol, but only slightly soluble in acetone, benzene, chloroform, and ether. Formaldehyde gas is flammable and forms explosive mixtures with air and oxygen.

Ignition temperature	572°F
Vapor density (air = 1)	1.067
Explosive limits (% by volume in air)	Lower 7 Upper 73

Formaldehyde Solutions (37 per cent). The most common commercial form of formaldehyde is an aqueous solution containing 37 per cent by weight dissolved formaldehyde plus sufficient methanol, as a stabilizer, to prevent precipitation of the solid polymer. USP formaldehyde contains not less than 37 per cent formaldehyde by weight with a variable percentage of methanol (usually 6 to 15 per cent by weight). Typical analyses of USP formaldehyde are:

Appearance	Clear, colorless liquid
Sp. gr.	(25/25°C) 1.0812 to 1.0984 (depending on methanol content)
Methanol content	6.0 to 12.5 per cent by weight
Acidity	About 0.02 per cent (as formic acid)
*p*H	About 3.5

37 per cent by weight formaldehyde solution containing the indicated percentage of methanol has the following properties:

Methanol Content, weight per cent	Flash Point, Closed Cup	Precipitation Temperature *
6		13°C (55°F)
8	152°F	9°C (48°F)
10	147°F	5°C (41°F)
12	133°F	0°C (32°F)

There are also available commercially, 30 and 37 per cent formaldehyde solutions which contain less than 1 per cent methanol. The 37 per cent "methanol-free" solution has the following typical analyses or general properties:

Appearance	Clear, colorless solution
Sp. gr.	(25/25°C) 1.1119
Methanol content	About 0.4 per cent by weight
*p*H	About 3.0
Flash point	185°F
Precipitation temperature	20°C (68°F)
B.P.	101°C
Ignition temperature	*ca.* 806°F

Formaldehyde Polymers (95 to 99 per cent). The two principal polymers of formaldehyde are paraformaldehyde (linear polymer of varying composition containing a mixture of polyoxymethylenes) and trioxane (cyclic trimer of definite composition).

Paraformaldehyde, $HO(CH_2O)_nH$ (n = approximately 8 to 50).

Appearance	White powder or granules having an odor of formaldehyde
Formaldehyde content	95 to 97 per cent by weight
Melting range	120 to 160°C

Soluble in dilute acid and alkali, dissolves slowly in cold water (more rapidly in hot water), and insoluble in acetone.

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* At or above the indicated temperatures, formaldehyde solutions remain clear for at least 24 hr. For longer periods of time, formaldehyde solutions must be maintained above these temperatures to prevent precipitation.

Trioxane $(CH_2O)_3$. Colorless crystals with a pleasant characteristic odor resembling chloroform; pure trioxane has no formaldehyde odor.

Mol. wt.	90.05	M.P.	61 - 62°C
Sp. gr. (molten)	1.17 65/20°C	B.P.	114.5–115.0°C

Readily soluble in virtually all organic liquids such as alcohols and ethers, except lower aliphatic hydrocarbons such as petroleum ether. Soluble in water (20 g per 100 g at 20°C); miscible in all proportions with hot water. Molten trioxane is an excellent solvent for organic materials such as phenol, naphthalene, urea, and, with 20 per cent water, the protein: zein.

Trioxane is very stable at ordinary temperatures and can be distilled without decomposition. It is relatively inert to water, alkali, and weak acids, but easily depolymerizes in the presence of small percentages of strong acids to give formaldehyde. It sublimes readily, forming colorless needles or rhombohedral crystals which are soft and pliant. Trioxane is combustible and ignites instantly, burning with a hot, nonluminous, clean, odorless flame. It is also very volatile at ordinary temperatures having a vapor pressure of 13 mm Hg at 25°C.

Flash point (closed cup)	100°F
Explosive limits (% by volume in air)	Lower 3.5
	Upper 28.7

Grades. USP formaldehyde solution (37 per cent), methanol-free formaldehyde solution (37 per cent), paraformaldehyde (95 to 97 per cent), and trioxane (99 per cent).

Containers and Regulations. Solutions: tank cars and trucks (72,000 lb), drums (475 lb), barrels (450 lb), kegs (125 lb), carboys (100 lb), and bottles. Stainless steel, rubber-, lacquer-, or glass-lined steel, and glass are used for materials of construction of the foregoing. Paraformaldehyde and trioxane: tightly sealed barrels, fiber drums, and bottles. Formaldehyde solutions and vapor have an irritating odor, which is intolerable in high concentrations. The maximum permissible concentration is about 10 ppm by volume, which is sufficient to cause lacrimation. Vapor and solution contact often cause severe dermatitis in sensitized persons. Paraformaldehyde has about the same hazards, and proper precaution should be taken. Trioxane exhibits none of the irritating properties of the foregoing. No ICC shipping label is required.

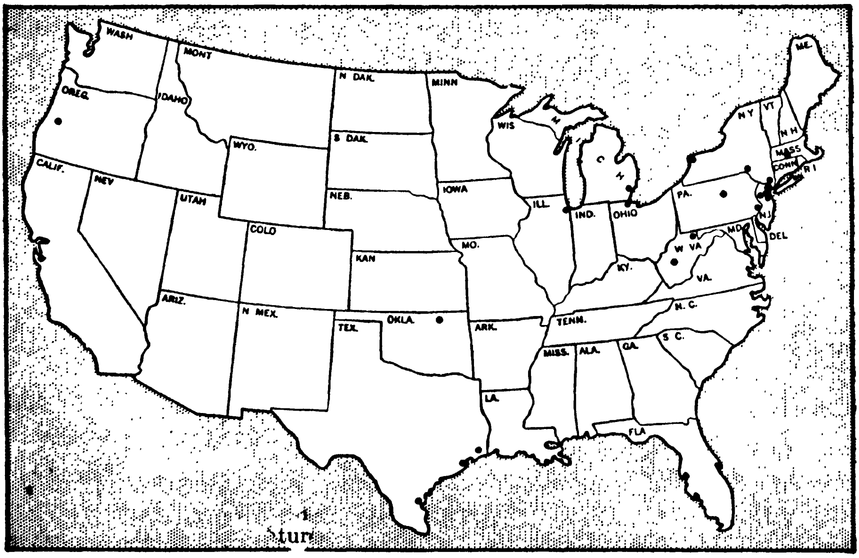
Economic Aspects

Formaldehyde processes may be classified into two types: (1) oxidation of methanol, and (2) oxidation of paraffin hydrocarbons. The second class includes both those using methane as raw material and those in which higher hydrocarbons, ethane, propane, and butane, are oxidized to yield several products of which one is formaldehyde (see *Acetaldehyde, Methanol*).

Comparison of the processes with respect to plant investment required is rather difficult, particularly since variations in operating procedures result in variable amounts of joint products in the hydrocarbon oxidation processes. In general, methanol oxidation plants are cheaper than others. A plant to produce 40,000,000 lb of 37 per cent formaldehyde solution yearly costs about $16,000 per 1,000,000 lb of 100 per cent formaldehyde, whereas hydrocarbon oxidation plants cost $130,000 to $175,000 per 1,000,000 lb annual production. The latter plants must, of course, receive credit for by-products, and the former should probably be charged with cost of a methanol plant to put both processes on the same basis.

The competitive situation between the various hydrocarbon oxidation processes is even more complex. Except for the methane oxidation process, experience with the various processes using hydrocarbons as raw material has been limited to pilot plants and recently built commercial plants. These processes received considerable impetus during World War II because of the great demand for formaldehyde for hexamethylenetetramine and pentaerythritol and the high requirements of methanol plants for critical metals.

The demand for formaldehyde for synthetic resins will undoubtedly increase, and so production is expected to remain at a high level.

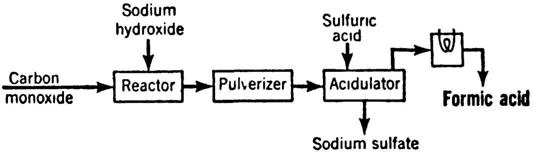


Location of Formaldehyde Plants

FORMIC ACID

HCOOH

From Sodium Formate



Reaction

$$CO + NaOH \rightarrow HCOONa$$

$$2HCOONa + H_2SO_4 \rightarrow 2HCOOH + Na_2SO_4$$

90–95% yield

Material Requirements

Basis—1 ton formic acid (90%)

Sodium hydroxide	1,950 lb
Carbon monoxide	1,450 lb
Sulfuric acid	2,300 lb

Process

Sodium hydroxide (97 to 98 per cent) is charged into a jacketed, agitated, autoclave (reactor), or into a packed tower. Carbon monoxide, usually obtained by the incomplete combustion of coke followed by the removal of carbon dioxide, is reacted with the caustic soda at 150 to 200°C under a pressure of 100 to 150 psi. The resulting reaction product is essentially crude sodium formate.

This reaction product, or sodium formate obtained as a by-product in other processes, may be acidified with dilute sulfuric acid and the resulting formic acid distilled off. However, only dilute formic acid (below 75 per cent) can be obtained by distillation because of the proximity of the formic-acid and water boiling points. The addition of concentrated sulfuric acid to dry sodium formate results in quite extensive decomposition with formation of carbon monoxide.

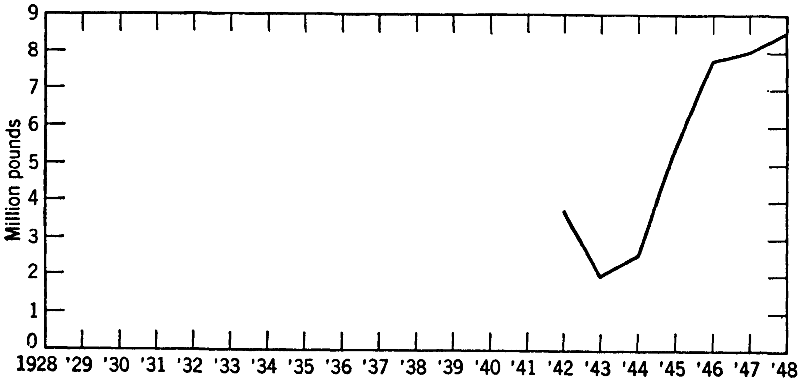
This decomposition is minimized by adding concentrated sulfuric acid to a slurry of powdered sodium formate in a sufficient quantity of preformed formic acid (85 to 90 per cent). The liberated formic acid of 85 to 90 per cent strength is separated from the sodium sulfate by any convenient method such as distillation. The yield based on the sodium hydroxide charged is 90 to 95 per cent.

From Methyl Formate

Formic acid may also be produced by the acid hydrolysis of methyl formate. Methanol and carbon monoxide are reacted at about 200°C under a pressure of 25 to 50 atm to give methyl formate. The formate is converted into dilute formic acid and methanol by the action of water and catalytic amounts of sulfuric acid. Essentially, anhydrous or concentrated formic acid may be obtained by subjecting methyl formate to reaction with glutaric or oxalic acid while admixed with an esterification catalyst such as sulfuric acid. Formic acid is liberated, and the formed methyl esters of the dibasic acid are hydrolyzed with water to liberate methanol. The regenerated dibasic acid is recovered.

From By-Products

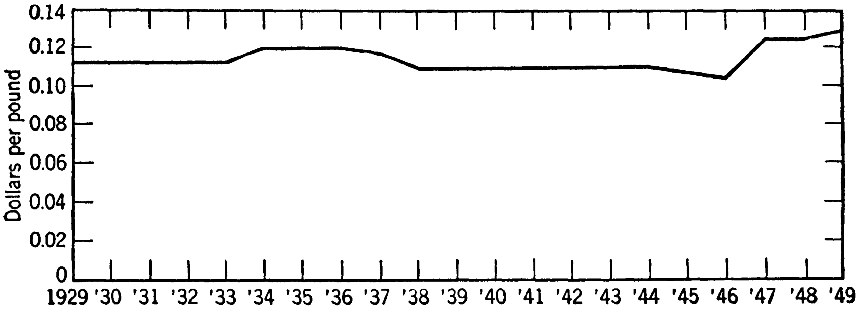
Formic acid is obtained as a by-product in the manufacture of acetaldehyde and formaldehyde by the catalytic oxidation of paraffin hydrocarbons. See *Acetaldehyde*, *Formaldehyde*.



Production—Formic-Acid Salts (No data on formic acid)

Use Pattern

Textile dyeing and finishing	No breakdown available
Leather tanning	
Formate esters	
Chemicals (syntheses)	
Rubber (latex coagulant)	
Protective coatings and resins	



Price—Formic Acid

Miscellaneous

Properties. Colorless, pungent smelling, highly corrosive, vesicatory liquid.

Mol. wt.	46.03	M.P.	8.4°C
Sp. gr.	1.220 20°C/4	B.P.	100.7°C

Weight per gallon 10.16 lb (20°C)

Soluble in all proportions at room temperature with water, alcohol, ether, and glycerol.

Flash point (closed cup)	156°F
Vapor density (air = 1)	1.59

Formic acid is irritating to the mucous membranes of the eyes, nose, and throat. Skin contact causes blisters and burns, which are usually slow in healing.

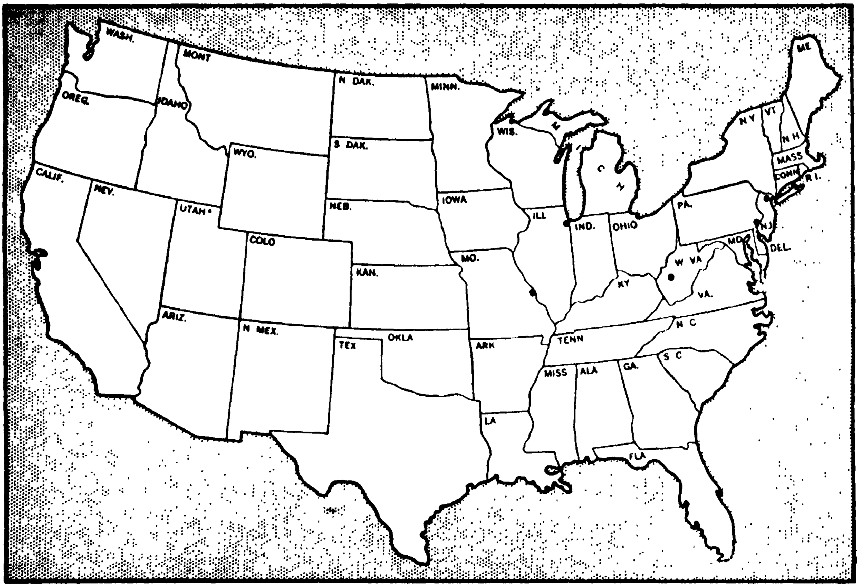
Grades. Technical (85 and 90 per cent) and N.F. (25 per cent).

Containers and Regulations. Glass carboys (150, 195 lb), drums, and glass bottles. Formic acid is very corrosive and must be handled in glass- or rubber-lined steel equipment. A white ICC shipping label is required.

Economic Aspects

Formic acid, as an industrial chemical, is much less important in sales volume than its homolog, acetic acid, although for many cases the two acids are interchangeable. Unless, however, formic acid presents a great advantage over acetic acid in a given case, the latter is commonly used because it is cheaper. In textile dyeing and finishing, and in the leather industry, formic acid is used, because it is a reducing agent as well as a relatively strong acid. At times the use of formic acid is indicated when subsequent removal by oxidation or heating is advantageous. The use of formic acid in the leather industry is expanding and may be expected to increase further.

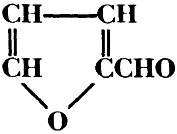
The particular formic-acid manufacturing process chosen by a given manufacturer depends largely on the raw-material situation. Methanol producers who make formic acid generally use the methyl formate process, whereas those also making oxalic acid prefer the carbon monoxide–alkali process because of interchangeability of equipment.



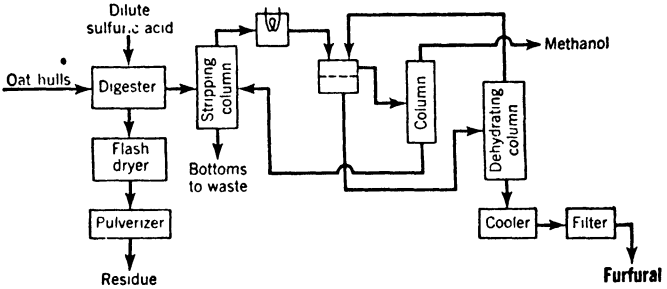
Location of Formic-Acid Plants

FURFURAL

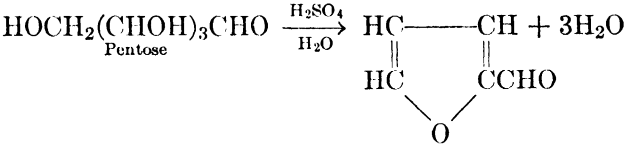
(FURFURALDEHYDE)



From Agricultural Residues



Reaction



70% yield

Material Requirements

Basis—1 ton furfural

Oat hulls	15,000 lb
Sulfuric acid (100%)	225 lb
Steam	40,000 lb

Process

Agricultural residues, such as oat hulls, which have a relatively high pentosan content are hydrolyzed to pentoses, which, in turn, split out water to form furfural. Although oat hulls give the highest yield of furfural (theoretically 20 per cent), other raw materials such as rice hulls (12 per cent), corn cobs (19 per cent), and cottonseed hull bran (17.5 per cent) are extensively employed.

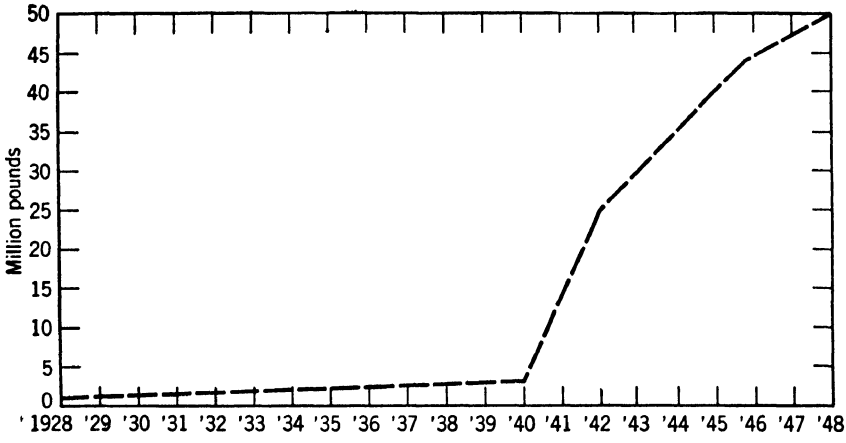
Ground-oat hulls (or similar material) are charged into spherical rotary digesters, together with dilute (5 to 10 per cent) sulfuric acid. The liquid–solid ratio approximates 0.25. Under 50 to 100 psi steam pressure, the materials are cooked approximately 2 hr. The main reaction produces furfural by hydrolysis of the pentosan content of the hulls. Side reactions occur, however, and produce small quantities of methanol, acetic acid, and other compounds.

The residue from the digester is flash-dried and pulverized. It is then used for fuel to produce steam or is sold as a fertilizer conditioner.

Vapors of the reaction products are carried out of the digester by the steam when the pressure is released and are passed into a stripping column. Here the furfural is azeotropically distilled and after condensation is run into a decanter. The top water layer is run into a column to recover methanol and acetaldehyde; the column bottoms, containing some furfural, are returned to the stripping column.

The bottom furfural layer from the decanter is dried by stripping off the water and methanol in a dehydrating column. After cooling, the furfural is passed through a pressure filter to give technical furfural of 99.5 per cent purity.

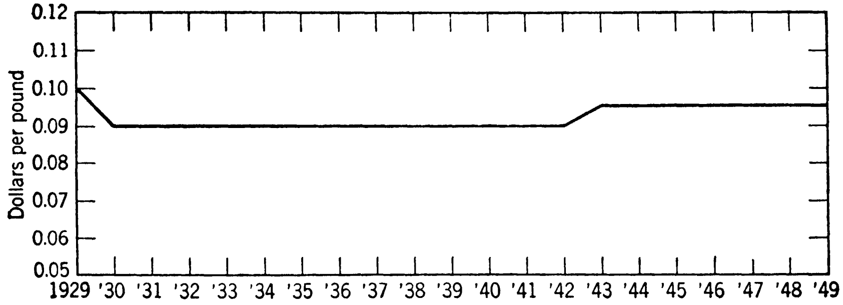
Refined furfural (special grade) is made by redistillation and decolorization of the technical product. An oxidation inhibitor is generally added to minimize darkening.



Production—Furfural (Estimated)

Use Pattern

	1947 (est.), per cent
Solvent refining	53
Chemical intermediate	11
Resins	23
Solvent	6
Miscellaneous	7
	100



Price—Furfural

Miscellaneous

Properties. Colorless, mobile liquid turning to reddish brown or dark amber on exposure to air and light. Characteristic penetrating odor.

Mol. wt.	96.08	M.P.	−38.7°C
Sp. gr.	1.1598 20°C/4	B.P.	161.7°C

Soluble in alcohol, ether, and benzene. Slightly soluble in water (8.3 g per 100 g at 20°C).

Flash point (closed cup)	140°F
Ignition temperature	739°F
Vapor density (air = 1)	3.31
Explosive limits (% by volume in air)	Lower 2.1

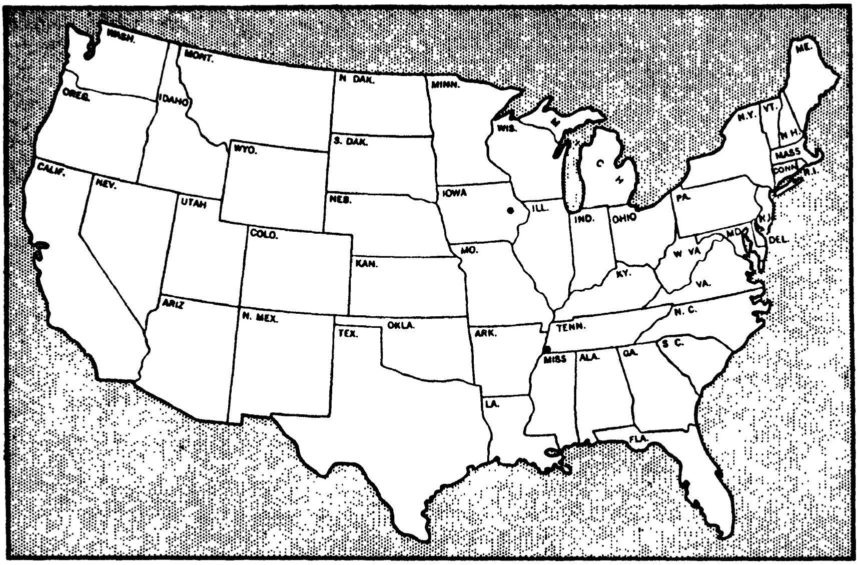
Grades. Technical (99.5 per cent) and refined or special grade.

Containers and Regulations. Tank cars, steel drums, cans, and bottles. No ICC shipping label required.

Economic Aspects

Wartime requirements for furfural chiefly in the refining of butadiene for the synthetic-rubber program resulted in the construction of a 24,000,000-lb plant (later operated at a capacity of 35,000,000 lb per yr), in addition to the single 15,000,000-lb prewar plant. The new plant was built in 1943 at a cost of $25,000,000.

The older plant had operated chiefly on oat hulls as a raw material and occasionally on corn cobs. The new (Memphis) plant used cottonseed hulls primarily but lately has changed to corn cobs. Various raw materials containing pentosans may be used, and whether an industrial by-product (oat hulls and cottonseed hulls) or a farm residue (corn cobs) is used depends on the economic situation. Generally, the cost of collection of corn cobs, even from elevators (where a great deal of corn is shelled), is such that industrial by-products are cheaper raw materials. In times of high grain prices, however, the value of oat hulls and cottonseed hulls for feed is so high that corn cobs are a cheaper raw material.



Location of Furfural Plants

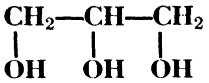
The major use of furfural prior to 1948 was in solvent-refining operations with fair quantities going into synthetic-resin manufacture. Indications are that future major uses will center around furfural derivatives, such as furoic acid, furfuryl alcohol, and hydrofuramide, which are now appearing on the market in increasing quantities. The conversion of furfural to tetrahydrofuran and subsequent conversion to adiponitrile for nylon manufacture are expected to constitute the major single use for furfural for the next few years. Recent development of a process to make nylon intermediates from butadiene may change this picture.

For a number of years, tremendous production of furfural and ethyl alcohol has been proclaimed the panacea for all farm problems by certain chemurgists, but the cost of collection of agricultural residues has prohibited such a program. The annual crop of corn cobs is about 16,000,000 tons, enough to yield 3,000,000,000 lb of furfural. The U. S. Department of Agriculture has recently initiated an extensive pilot-plant study on the conversion of agricultural residues to furfural and alcohol.

Acetaldehyde is recovered as a by-product in furfural manufacture. A considerable quantity of acetic acid is also produced in dilute solution but has hitherto not been recovered.

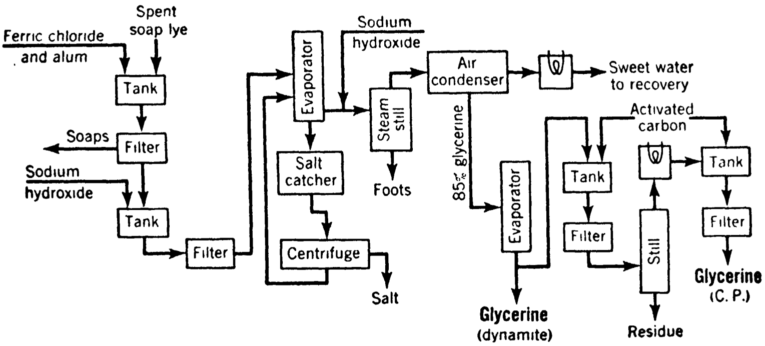
GLYCERINE

(GLYCEROL)



$$\underset{OH}{CH_2}-\underset{OH}{CH}-\underset{OH}{CH_2}$$

By-Product from Soap Manufacture



Reaction

$$C_3H_5(COOR)_3 + 3H_2O \rightarrow C_3H_5(OH)_3 + 3RCOOH$$

$$C_3H_5(COOR)_3 + 3NaOH \rightarrow C_3H_5(OH)_3 + 3RCOONa$$

75% yield (hydrolysis or saponification and recovery)

90% recovery (from spent soap lye)

Material and Utility Requirements

Basis—1 ton glycerine (plus 2.2 tons salt)

Spent lye (5% glycerine)	22 tons	Activated carbon	5–10 lb
Sodium hydroxide	200 lb	Steam	8,000 lb
Ferric chloride	110 lb	Electricity	10 kw-hr
Aluminum sulfate	22 lb		

Process

The hydrolysis or saponification of fats and oils in the manufacture of free fatty acids and soap yields glycerine as a by-product.

In the hydrolysis process, the mixed glycerides of various fatty acids (the main constituents of fats and oils) are split to give free fatty acids and glycerine. This may be accomplished by several processes: for example, the hydrolysis by water at ordinary pressures with the aid of a catalyst (Twitchell process), the high-temperature–high-pressure hydrolysis with or without a catalyst (autoclave process), and the continuous countercurrent hydrolysis at high temperatures and pressures with or without the aid of a catalyst (Ittner process).

The saponification method generally utilizes sodium hydroxide as the alkali and is operated batchwise or continuously to give soap and glycerine. In the older, more common batch processes, the saponified product is separated into soap and a mixture called spent soap lyes by graining with sodium chloride. The continuous process is operated at high temperatures and pressures to give a reaction mixture, which may be separated by mechanical means (passage through muslin-lined spraying chambers) into powdered soap and vapors of aqueous glycerine.

The hydrolysis and continuous saponification processes yield aqueous, salt-free solutions containing about 15 per cent glycerine. Generally, these solutions require very little chemical treatment (mere neutralization with lime or barium hydrate) and are concentrated by evaporation to give crude glycerine known as "88 per cent saponification crude." In the batch saponification process, spent soap lyes are obtained as by-products and must be chemically purified before recovery of glycerine. A typical spent lye contains 3 to 8 per cent glycerine, 5 to 15 per cent sodium chloride, water, and small quantities of alkali, soap, fatty acids, and other organic impurities. After chemical treatment, the spent lyes are concentrated to yield crude glycerine known as "80 per cent soap lye crude." Since the recovery of glycerine from spent soap lyes is a major source of supply and entails a more involved procedure, it is described in detail (see flowsheet).

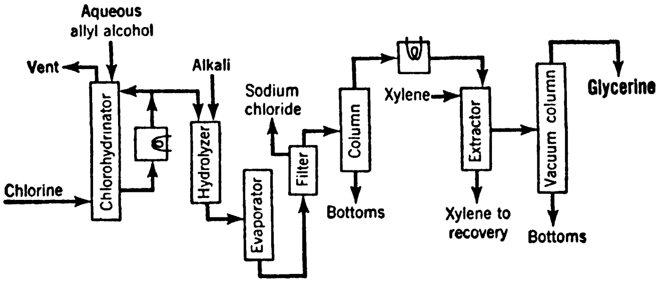
Spent lye, which has been allowed to cool and settle to remove much of the soap, is pumped into an open steel tank fitted with an agitator. Ferric chloride in solution is added in the required amount to form insoluble precipitates with the soap and carbonated alkali impurities. Approximately 5 lb ferric chloride per ton of lye is needed; an additional pound of aluminum sulfate (per ton of lye) is customarily used for low-grade lyes to obtain a more complete removal of impurities. Just enough hydrochloric acid is added to cause precipitation of the metallic soaps.

The slightly acid lyes are filtered and run into a second tank, where enough aqueous sodium hydroxide is added to bring them over to the alkaline side. After filtration the lye contains 4 to 10 per cent glycerine and 10 to 18 per cent salt. This material is concentrated in a double-effect evaporator which is provided with salt catchers. Much of the salt crystallizes during evaporation and is periodically dropped from the evaporator cone into the salt chambers. From here the salt is removed, centrifuged (or filtered on a Nutsch filter), washed, and returned to the soap plant for re-use. The evaporation is stopped when the glycerine content of the liquor has reached about 80 per cent. This crude product, 80 per cent soap lye crude, contains 4 to 11 per cent salt, about 0.1 per cent soap, and smaller amounts of organic impurities.

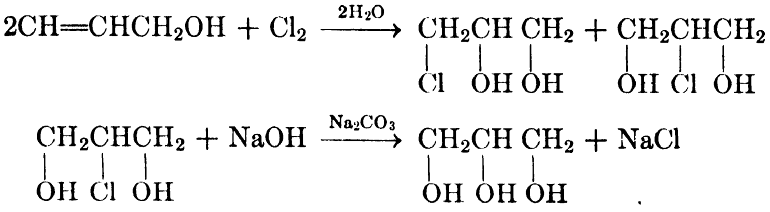
The crude soap-lye glycerine or crude saponification glycerine (from the hydrolysis plants) is refined by steam distillation under vacuum. The crude material is first made strongly alkaline to hold back fatty-acid impurities and is then charged into a direct-steam still. The vapors are condensed by passage through a series of air condensers and finally through a water-cooled condenser. Most of the glycerine is removed by the air-cooled condensers as 85 per cent refined glycerine; the water containing about 1 to 2 per cent glycerine is collected in the water-cooled condenser. This material, known as sweetwater, is treated separately by evaporation to remove the glycerine.

The 85 per cent refined glycerine is concentrated to give the 99 per cent dynamite grade. By decolorizing with activated carbon, a pale-yellow high-gravity or industrial grade may be obtained. USP or C.P. glycerine is produced by passing the dynamite grade of glycerine through activated carbon, redistilling, and then redecolorizing with activated carbon. This water-white product contains 95 to 98 per cent glycerine; the rest is water. The recovery yield of C.P. glycerine from spent soap lye is approximately 90 per cent.

From Allyl Alcohol or Chloride by Synthesis



Reaction



$$2CH{=}CHCH_2OH + Cl_2 \xrightarrow{2H_2O} \underset{Cl}{CH_2}\underset{OH}{CH}\,\underset{OH}{CH_2} + \underset{OH}{CH_2}\underset{Cl}{CH}\underset{OH}{CH_2}$$

$$\underset{OH}{CH_2}\underset{Cl}{CH}\underset{OH}{CH_2} + NaOH \xrightarrow{Na_2CO_3} \underset{OH}{CH_2}\underset{OH}{CH}\,\underset{OH}{CH_2} + NaCl\;.$$

90% yield

Material Requirements

Basis—1 ton glycerine (99%)

Allyl alcohol	1,560 lb	Sodium hydroxide	1,000 lb
Chlorine	960 lb	Sodium carbonate	100 lb

Process

The reaction of allyl alcohol and allyl chloride with aqueous chlorine or hypochlorous acid yields monochlorohydrin and dichlorohydrins, respectively. By the alkali treatment of these products, glycerine is obtained.

Dilute aqueous allyl alcohol (5 per cent) is fed into the top of a packed tower reactor countercurrent to gaseous chlorine. The tower is filled with the chlorine, which acts as the continuous phase while part of the aqueous alcohol is recirculated. By cooling the recirculating liquid the exothermic reaction is controlled so that a temperature of about 15°C is maintained. Approximately two volumes of the product are recycled per volume of alcohol feed.

The reaction product, consisting mostly of glycerol monochlorohydrins, is withdrawn from the reactor and fed into a hydrolyzer. Simultaneously, aqueous alkali, containing a mixture of about 10 per cent sodium hydroxide and 1 per cent sodium carbonate, is charged at approximately the same rate of feed, so that the autoclave hydrolyzer is maintained near capacity. At about 150°C and a contact time of 0.5 hr, crude glycerine results. The reaction product is withdrawn at about the same rate as the input and fed to an evaporator where crude glycerine is obtained. Sodium chloride crystallizes from the aqueous glycerine and is removed by filtration. The filtered liquor is distilled and condensed to yield about 90 per cent glycerine, 2 per cent unreacted allyl alcohol, and miscellaneous impurities. After extraction with xylene, which removes the organic chlorides, the material is fractionally distilled under vacuum to yield glycerine of more than 99 per cent purity. A yield of about 90 per cent is realized based on allyl alcohol.

It is also possible and supposedly preferable to produce glycerine directly from allyl chloride, thus eliminating the allyl alcohol step. As shown by the following principal reactions, more alkali is required for the hydrolysis:

$$CH_2{=}CHCH_2Cl + HOCl \rightarrow ClCH_2CH(OH)CH_2Cl$$

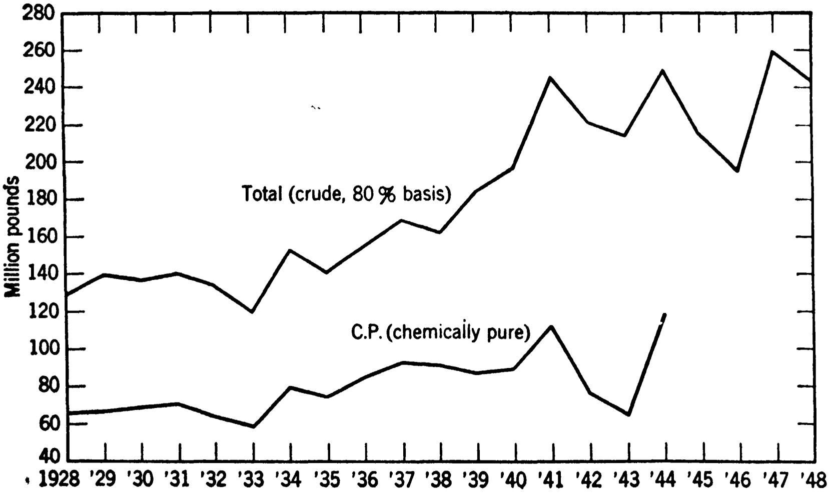
$$ClCH_2CH(OH)CH_2Cl + 2NaOH \rightarrow HOCH_2CH(OH)CH_2OH + 2NaCl$$

Different conditions are necessary for the chlorohydrination of allyl chloride, since the chloride is substantially water-insoluble, whereas the afore-mentioned allyl alcohol is water-soluble.

Allyl chloride may be reacted with hypochlorous acid to yield primarily glycerol dichlorohydrin. The chloride should be well dispersed in an excess of water, and the reaction is generally carried out at 25 to 30°C. The product is treated in a manner similar to the previously mentioned monochlorohydrin hydrolysis to yield crude glycerine. Using the same methods of concentration and purification, a comparable grade of glycerine is obtained in about a 90 per cent yield based on allyl chloride.

From Sugars by Fermentation

Glycerine is produced in small amounts in the fermentation of various sugars to produce alcohol. Although the glycerine is generally lost in the still residue during the alcohol distillation, the processes for pro-

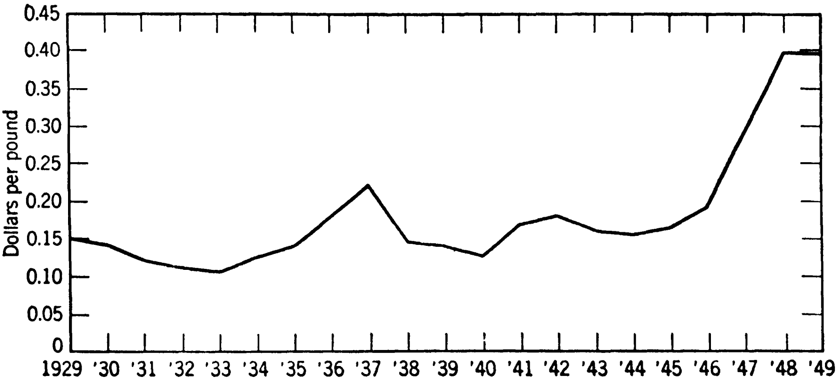


Production—Glycerine

ducing glycerine as the main product are very similar to those used in ethyl alcohol production. For this reason, the reader is referred to *Ethyl Alcohol*. However, the course of the fermentation is changed generally by adding sodium sulfite to the mash and keeping the fermentation on the alkaline side. As high as a 30 per cent glycerine yield, with alcohol as a by-product, is claimed. For example, 50 parts of sodium-acid sulfite are slowly added to a fermentation batch containing 100 parts of sugar, 2 parts of ammonium phosphate, 2 parts of magnesium sulfate, 10 parts of fermentation yeast (race M), and 1,000 parts of water. Air is blown through the ferment, and the *p*H is maintained on the alkaline side by adding alkali. The crude glycerine obtained is very poor in quality, and drastic methods of refining are necessary to produce satisfactory grades. On a pilot-plant scale the stillage has been refined by evaporation to 50 per cent solids, followed by flash distillation from a spray in a vacuum chamber, by dialysis, and by liquid-liquid extraction. The process has never been used in the United States except on a pilot-plant scale.

Use Pattern

	1947 (est.), per cent
Synthetic resins	20
Rayon and cellophane	15
Dynamite	15
Tobacco	15
Miscellaneous	35
	100



Price—Glycerine

Miscellaneous

Properties. Clear, colorless, sirupy, odorless hygroscopic liquid with a sweet, warm taste.

Mol. wt.	92.09	M.P.	17.9°C
Sp. gr.	1.260 20°C/4	B.P.	290°C

Weight per gallon	10.50 lb (20°C)

Soluble in water and alcohol. Insoluble in benzene, chloroform, ether, and petroleum ether. Absorbs moisture from the air, also sulfur dioxide and hydrogen sulfide, if present.

Flash point (closed cup)	320°F
Ignition temperature	739°F
Vapor density (air = 1)	3.17

Grades. USP and C.P.: colorless, used in foods and pharmaceuticals (95 to 98 per cent). High gravity: pale yellow, for industrial purposes (99 per cent). Dynamite: yellow, for explosives manufacture (99 per cent). Yellow distilled: yellow, for industrial purposes (99 per cent). Crude: saponification (88 per cent) and soap lye (80 per cent).

Containers and Regulations. Tank cars (aluminum and steel), drums, tins, and bottles. No ICC shipping label required.

Economic Aspects

Glycerine is primarily a by-product of soap manufacture (roughly 60 lb glycerine per ton of soap), and, accordingly, supply and price are governed largely by demand for the main product: soap. Crude glycerine is produced by over 200 soap makers and producers of fatty acids. The crude may be sold as such to refineries or refined on the premises to dynamite grade or C.P. glycerine. Soap manufacturers normally produce 85 per cent of United States requirements for glycerine. Of the total refined output, 60 per cent is C.P. grade, and 40 per cent dynamite and other grades.

The two chief threats to by-product glycerine production are (1) the competition of synthetic detergents, use of which tends to reduce soap production, and (2) synthetic-glycerine production. The possibility of developing a commercially feasible process for manufacturing soaps by the oxidation of paraffin to fatty acids must also not be forgotten. In general, the two nonfat processes, fermentation of sugars, and synthesis from propylene, can compete only with moderate- and high-priced glycerine. The possibilities of the two processes are such, however, that they tend to keep a ceiling on soap-lye glycerine price. It is not inconceivable that technical advances in the nonfat processes will make these processes competitive with resultant lower average glycerine prices.

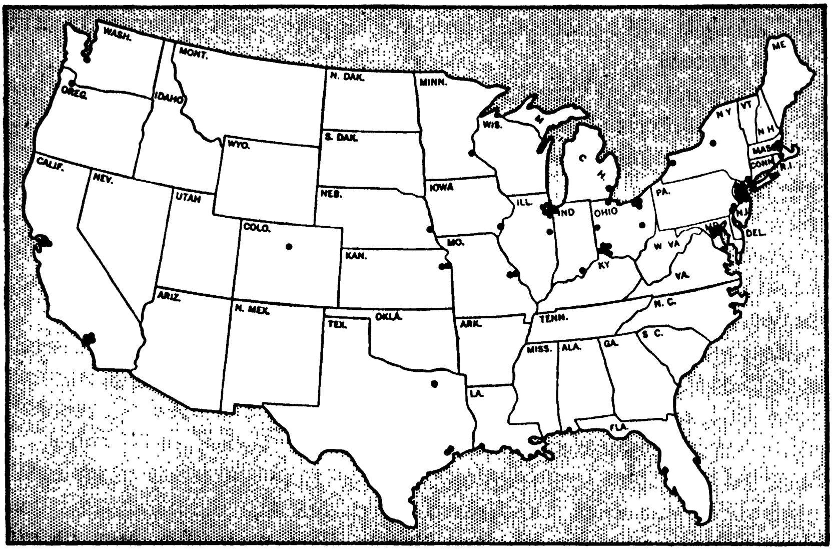
The chief problem in the manufacture of fermentation glycerine is recovery and purification of glycerine from the fermentation liquors; the number of steps required in the synthetic process tends to increase operating costs. Further development of the allyl chloride process (see *Allyl Alcohol*) will be reflected, however, in potentially cheaper glycerine by this process.

Another potential threat to soap-lye glycerine is a process based on the hydrogenolysis of sugars. During World War II, the Germans built a 180-ton-per-month plant in which dextrose was hydrogenated to produce a mixture of glycerine, propylene glycol, and higher alcohols. The process appears to have interesting possibilities.

Glycerine enjoys very wide use in industry because of both its chemical and its physical properties. Because of this wide use, glycerine production is regarded by some as a good index of business conditions. Its greatest use as a chemical is in the manufacture of alkyd resins, whereas its chief uses because of physical properties center around its moistening, lubricating, and softening characteristics. In all fields it must compete with other polyhydric alcohols such as pentaerythritol and sorbitol. A concerted effort was made several years ago to obtain larger usage in the automobile permanent "antifreeze" field, but the public showed considerable preference for ethylene glycol. This preference may be due largely to differences in advertising methods. The demand for "more essential" uses during the war further limited its use in this market.

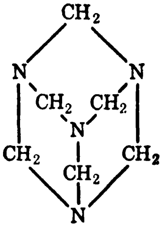
The size and cost of glycerine-recovery units in soap factories varies widely, the former being dependent on the amount of soap produced and the amount of glycerine left in the soap, and the latter on the type of recovery equipment used. The popular recovery systems differ only in detail and appear to be competitive, but operations are not always carried out most efficiently. Many soap makers are said to lose 20 per cent of the theoretical glycerine content in recovery operations. Others report efficiencies that result in only a 5 per cent loss. The installation of recently developed high-pressure fat-splitting processes in the soap industry, thus avoiding the need for soap kettles and salting out of the soap, will eventually simplify glycerine recovery by obviating the necessity for cumbersome salt-removal equipment. It is estimated that the smallest economic recovery unit is one with an annual capacity of 100,000,000 lb.

It is also estimated that a complete synthetic plant would cost about $200,000 per 1,000,000 lb annual capacity for a plant in the neighborhood of 25,000,000 lb yearly production. One synthetic plant started operations in 1948. A complete fermentation plant would cost less than one half as much. In both cases, credit must be taken for by-products. The fermentation process yields 1 gal of 95 per cent alcohol for each 3 lb of glycerine; by-products from the synthetic glycerine process are discussed under *Allyl Alcohol.*

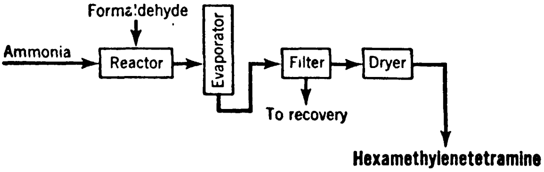


Location of Major Glycerine (Crude and Refined) Plants

HEXAMETHYLENETETRAMINE



From Formaldehyde and Ammonia



Reaction

$$6CH_2O + 4NH_3 \rightarrow (CH_2)_6N_4 + 6H_2O$$

95% yield

Material Requirements

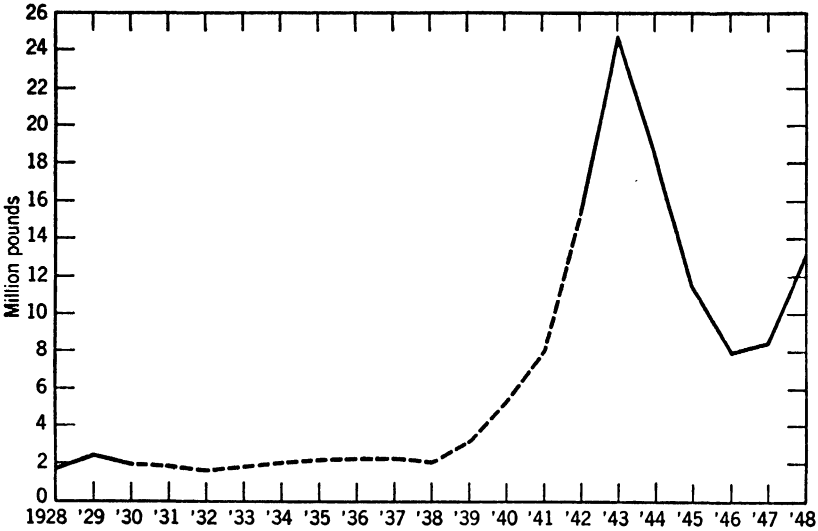
Basis—1 ton hexamethylenetetramine

Formaldehyde (37%)	7,150 lb
Ammonia (100%)	1,100 lb

Process

Aqueous 30 or 37 per cent (by weight) methanol-free formaldehyde is charged into a reaction kettle. Ammonia gas, in about a 3-to-2 formaldehyde–ammonia mole ratio, is slowly added under the surface of the solution with efficient agitation. The temperature during addition is maintained at 20 to 30°C. After the ammonia has been added in slight excess, the reaction mixture is transferred to a vacuum evaporator. Here the solution is concentrated until most of the water has been removed and crystallization has taken place. The damp crystals are centrifuged, washed with water, and dried to yield technical hexamethylenetetramine.

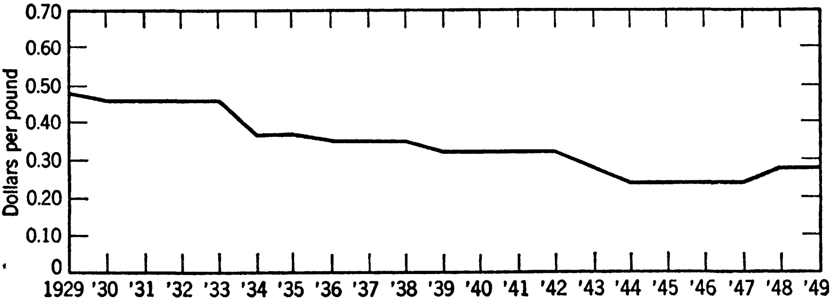
The mother liquor and washings are reworked back into the system to recover the dissolved hexamethylenetetramine. The technical material may be recrystallized from alcohol or be precipitated from aqueous solution by saturation with ammonia to give USP hexamethylenetetramine. The over-all yield is 90 to 95 per cent based on the weight of formaldehyde charged.



Production—Hexamethylenetetramine

Use Pattern

	1947 (est.), per cent
Plastics and resins	80
Other (includes medicinals)	20
	100



Price—Hexamethylenetetramine

Miscellaneous

Properties. White crystalline powder with a sweet taste. In the pure form, it is colorless and odorless.

Mol. wt.	140.19	M.P.	Does not melt
Sp. gr.	1.270 (25°C)	B.P.	Sublimes in vacuum at 230 to 270°C

Soluble in water (46.5 g per 100 g at 25°C, 43.4 g per 100 g at 70°C), alcohol, and glycerine. Slightly soluble in ether, chlorinated aliphatics, and aromatic hydrocarbons.

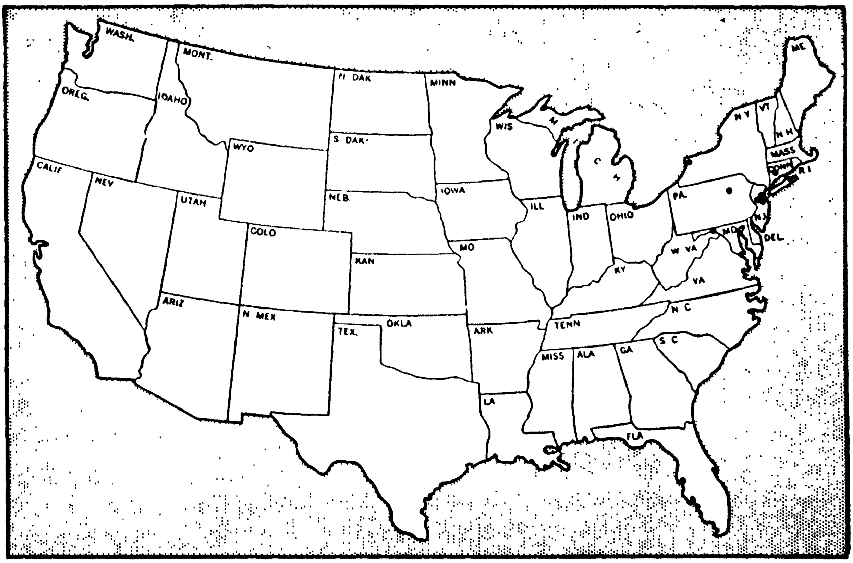
Flash point (closed cup) 482°F
On ignition, it burns with a pale-blue flame.

Grades. Technical (*ca.* 99 per cent), and USP (*ca.* 99.5 per cent).

Containers and Regulations. Fiber drums (350, 100 lb), barrels (200 lb), and bottles. Dermatitis is frequently encountered in the manufacturing and handling of hexamethylenetetramine. No ICC shipping label required.

Economic Aspects

Hexamethylenetetramine production soared during World War II because of its use in the manufacture of the explosive RDX, the chief component of "blockbusters." During the latter part of the war, RDX



Location of Hexamethylenetetramine Plants largely replaced TNT in aerial bombs. Before the war, hexamethylenetetramine was used principally in phenol–formaldehyde plastics and pharmaceuticals, and it is to these markets that it has returned since the war, although some RDX is said to be used in blasting caps. Manufacturing capacity is greatly inflated; albeit the greatest percentage is in Government-owned ordnance plants. Some new and expanded uses will undoubtedly be found, but there is considerable doubt that peacetime production will ever be as high as production was during World War II.

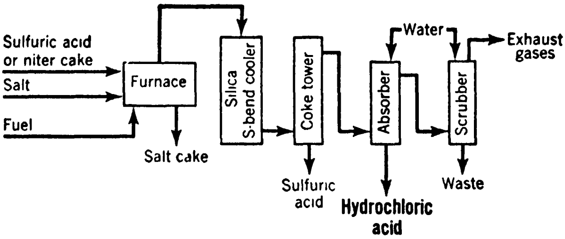
The capacities of normal peacetime plants vary from 2,000,000 to 10,000,000 lb per yr. A complete plant may be expected to cost in the neighborhood of $375,000 per 1,000,000 lb annual capacity.

As would naturally be expected, most plants are tied in with formaldehyde plants, since the latter is the raw material for the former.

HYDROCHLORIC ACID

HCl

From Salt



Reaction

$$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4$$

$$NaCl + NaHSO_4 \rightarrow HCl + Na_2SO_4$$

98% yield

Material Requirements

Basis—1 ton hydrochloric acid (20°Bé)

and 1,260 lb salt cake from sulfuric acid or 2,840 lb salt cake from niter cake

Salt	1,050 lb
Sulfuric acid (100%)	945 lb
or	
Niter cake	2,630 lb
Coal	740 lb

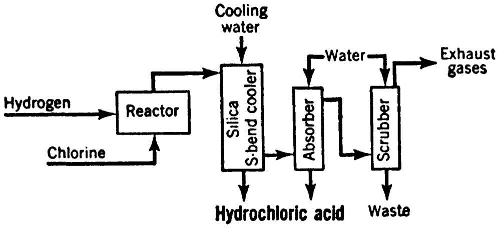
Process

Salt and 60°Bé sulfuric acid (slight excess) or salt and an equivalent amount of niter cake (see *Nitric Acid*) are charged to a furnace equipped with a rake agitator (Mannheim furnace), where the reacting mass is slowly heated to a temperature just below fusion (843°C). Hydrogen chloride is evolved and led through a cooling and condensing system to the absorbers. Salt cake (crude sodium sulfate) is continuously discharged from the periphery of the furnace.

The combustion gases, containing hydrogen chloride (approximately 30 per cent HCl), leave the furnace at about 840°C, pass into silica S bends (coolers) externally cooled with water and leave the coolers at about 38°C. The cooled gases then pass through a coke-packed tower, in which sulfuric-acid mist and any solid particles present are removed, and thence to another series of silica S bends (Tyler absorbers), where the hydrogen chloride is absorbed by water to produce hydrochloric acid. Exhaust gases from the absorber are scrubbed with water and discharged to the atmosphere. The most recently designed plants have made use of impervious graphite and structural plastics for absorbers and coolers.

A few plants use the Laury furnace, a horizontal rotary kiln, in which the reacting mass comes into contact with fuel combustion gases. These gases, containing as little as 5 per cent hydrogen chloride, leave the furnace at 300°C, and are cooled and then recovered in the manner described previously.

From Chlorine and Hydrogen



Reaction

$$H_2 + Cl_2 \rightarrow 2HCl$$

85–90% yield

Material Requirements

Basis—1 ton hydrochloric acid (20°Bé)

Chlorine	618 lb
Hydrogen	22.1 lb

Process

Chlorine is burned in a slight excess of hydrogen to produce hydrogen chloride. Several types of burners are used: for example, the silica burner, the ceramic-lined burner, the graphite burner, and the water-jacketed steel burner. The last-mentioned burner cannot, of course, be used with wet gases. Recently, a submerged combustion burner, operating beneath a surface of muriatic acid, has been developed. The burner gases, practically pure hydrogen chloride, are cooled, absorbed, and scrubbed in a system essentially the same as that used in the salt process. The purifying coke tower, however, is omitted, and in some systems (where the gas concentration approaches 100 per cent HCl) the scrubber may be omitted. Strong hydrochloric acid (22°Bé) is removed directly from the bottom of the cooler by means of a trap, and weak acid (18°Bé) leaves the bottom of the absorber. Recently installed absorbers have been built of tantalum and structural carbon as well as silica. This process readily gives a water-white product.

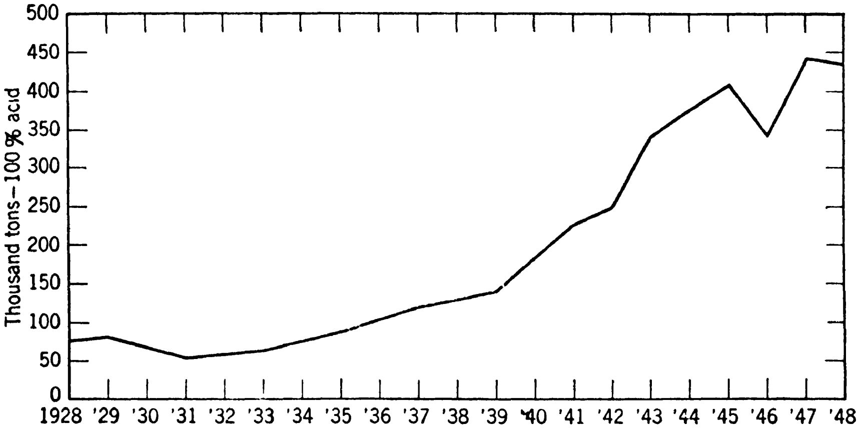
Hydrochloric acid is also made by burning chlorine in methane or water gas, according to the following equation:

$$2Cl_2 + CH_4 + \text{Air} \rightarrow 4HCl + CO_2$$

The recovery system is the same as that used in the chlorine–hydrogen process.

By-product hydrochloric acid is the result of large-scale organic syntheses: for example, the chlorination of benzene to yield chlorobenzene. The exhaust gases from the reaction are purified to remove excess chlorine and volatile organic constituents and are then absorbed in the manner described previously to produce hydrochloric acid. See *Amyl Alcohol* or *Chlorobenzene* for further details.

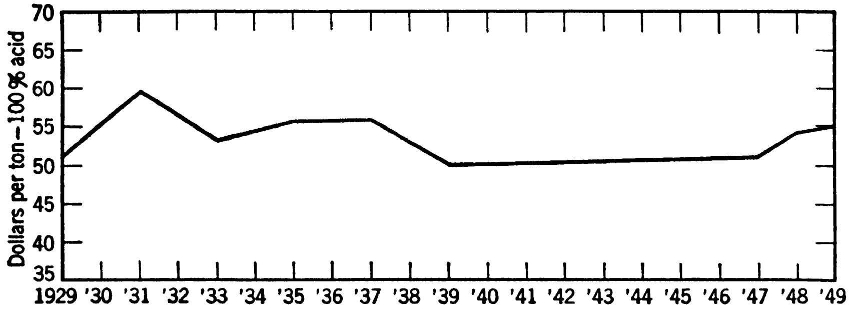
Anhydrous hydrogen chloride (containing 99.8 per cent HCl) is available in steel cylinders. It may be prepared by passing the hot (260°C) burner gases over cold anhydrous calcium chloride. The dry hydrogen chloride is then compressed and charged into cylinders. A yield of 99 per cent of the hydrogen chloride supplied by the burners is realized.



Production—Hydrochloric Acid

Use Pattern

Dyes and organic chemicals Petroleum isomerization (anhydrous HCl) Acidizing oil wells Heavy chemicals Glue Textiles Soap Glucose Miscellaneous *	No breakdown available



Price—Hydrochloric Acid

Miscellaneous

Properties. Hydrochloric acid is a solution of hydrogen chloride in water. Pure hydrogen chloride is a colorless, pungent poisonous gas at ordinary temperatures and pressures.

Mol. wt.	36.47	M.P.	−112°C
Sp. gr. (0°C)	1.268 (air = 1)	B.P.	−35°C
Density (0°C)	1.639 gpl		

It is liquefiable under a pressure of 82 atm at 51°C. At atmospheric pressure, the liquefied gas boils at −85°C and has a specific gravity of 1.194.

Easily soluble in alcohol and ether as well as in water. A constant-boiling mixture of hydrogen chloride and water contains 20.24 per cent HCl and boils at 110°C at 760 mm pressure.

Grades. Technical, C.P. and USP. The usual technical or commercial grade, commonly known as muriatic acid, is yellowish in color.

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* Includes steel cleaning, naval stores, glass and ceramics, oils and fats, and resins and plastics.

The C.P. and USP grades (20°Bé) are colorless and low in metallic and other impurities. The common grades of commercial acid are:

Degrees Baumé	Percentage HCl	Specific Gravity
16	24.5	1.124
18	28.0	1.142
20	32.0	1.160
22	36.0	1.179

Containers and Regulations. Rubber-lined tank cars, rubber-lined barrels and drums, carboys, and bottles. Glass-lined containers are also used. Anhydrous hydrogen chloride is shipped in steel cylinders under pressure. A green ICC shipping label is required. The acid is a highly corrosive liquid, and a white ICC shipping label is required.

Economic Aspects

Hydrochloric acid is usually manufactured as one of a large number of heavy chemicals or inorganic acids made by the same establishment. The exception is by-product acid recovered in the organic chlorination industry, often because of laws prohibiting the discharge of acid gases to the atmosphere.

The classical method of manufacture is the salt–sulfuric-acid process in which salt cake is recovered as a by-product. In recent years, the demand for water-white acid has led to the establishment of the chlorine–hydrogen burner process, which is gradually replacing production from the old furnace installations. The future competitive status of the two processes will depend on the cost of chlorine and the market for salt cake. In general, the burner process can be operated more economically on a small scale than the furnace process.

Both processes will receive competition from by-product hydrochloric acid, production of which has increased because of the gaining importance of organic chlorination processes and the development of simple structural carbon- and tantalum-recovery units. Considerably more acid would be recovered if there were a market near the point of production.

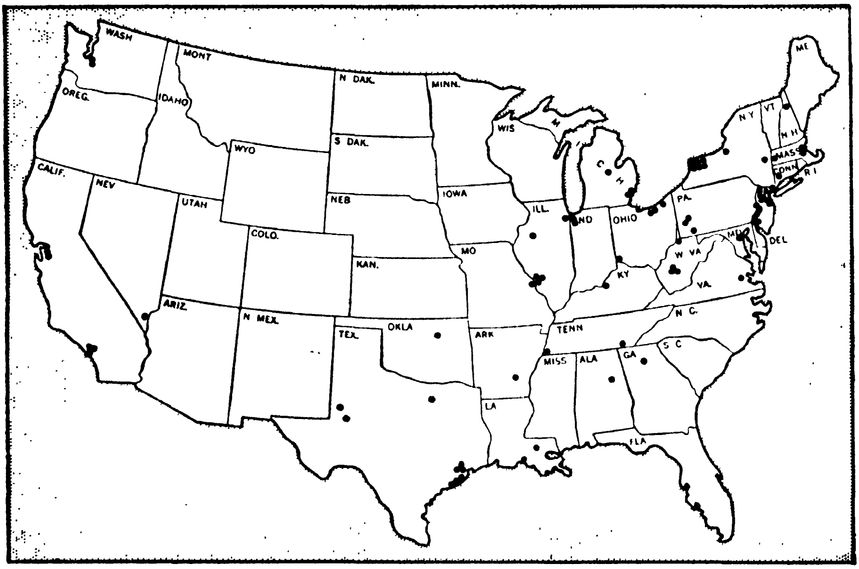
Competition between the several furnace processes centers around furnace design. Both Mannheim (mechanical-muffle) and Laury (rotary) furnaces are used in the United States, with the former in greater use. The old pot-and-muffle process is considered obsolete.

In 1939 relative production was 67 per cent from salt, 13 per cent from chlorine, and 20 per cent as by-product. In 1947 the respective percentages were 40, 20, and 40.

The production of hydrochloric acid is considerably less than that of sulfuric and nitric acids. It is commonly used for its acid characteristics where its volatility, nonoxidizing characteristics, high acidity per unit weight, and ease of neutralization are advantageous. Its chief drawbacks are cost and extreme corrosiveness to metals. Much greater use would accompany the development of a cheap, easily machinable corrosion-resistant alloy.

Plant sizes usually vary from 2,000 to 50,000 tons annually, with the smallest plants limited to by-product production. A normal Mannheim furnace has a capacity of 12,000 tons, and a Laury furnace 36,000 tons. By-product gas-recovery plants in the range of 10,000 to 20,000 tons annually cost $4 to $15 per ton capacity, depending on gas concentration and purity.

Demand for anhydrous hydrogen chloride increased markedly during World War II for the chlorination of unsaturated organic compounds and butane isomerization. Various processes were used and proposed; one of the most interesting was the Grasselli process starting with chlorosulfonic acid to produce 2 lb of 66°Bé sulfuric acid for each pound of hydrogen chloride.

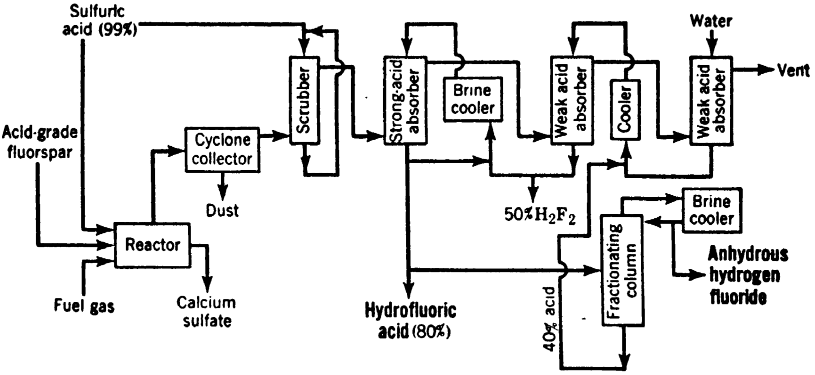


Location of Hydrochloric-Acid Plants

HYDROFLUORIC ACID

H_2F_2

From Fluorspar and Sulfuric Acid



Reaction

$$CaF_2 + H_2SO_4 \rightarrow H_2F_2 + CaSO_4$$

90–95% yield

Material Requirements

Basis—1 ton anhydrous hydrogen fluoride

Fluorspar (98% CaF_2)	4,000 lb
Sulfuric acid (99%)	5,500 lb

Process

By treating fluorspar (calcium fluoride) with concentrated sulfuric acid in a furnace, hydrogen fluoride gas is evolved, leaving a residue of calcium sulfate. After absorption in water, the gas is concentrated by distillation to yield various grades of aqueous and anhydrous hydrofluoric acid.

Crude fluorspar, fluorite, as it comes from domestic mines, varies in calcium fluoride content from about 50 to 90 per cent. To be suitable for acid production the ore must be upgraded. This is usually done by flotation processes and results in an acid-grade fluorspar, containing about 98 per cent calcium fluoride, 1 per cent silica, 0.03 per cent sulfur, and less than 0.5 per cent moisture.

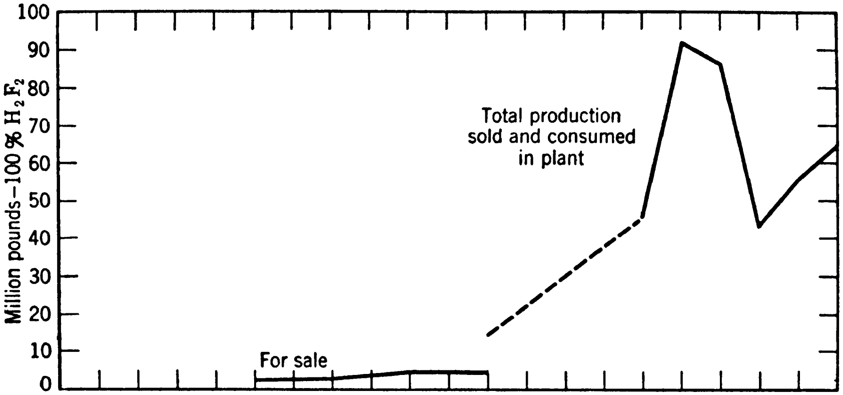
The acid-grade fluorspar, in finely powdered form, is withdrawn from storage silos and transferred by air conveyers to steel conical-bottom hoppers. From here it is fed continuously along with concentrated (98.5 to 99 per cent) sulfuric acid into a rotating (about 1 rpm) retort enclosed in a brick setting. The furnace is fired by producer gas or a similar fuel in such a manner that the hot gases do not strike the shell directly. The retort, a cylindrical mild-steel shell (0.75 in. thick), about 40 ft long and 6 ft in diameter, has a pitch of about 1.2 degrees.

The raw materials are fed into the retort at a ratio of 1 mole of fluorspar to 1.3 moles of acid. Calcium sulfate residue, containing 1 per cent or less unreacted fluorspar, is discharged continuously and amounts to about 1.75 times the weight of the spar charge. From the feed end of the retort, gaseous hydrogen fluoride (70 to 75 per cent H_2F_2) is withdrawn at a temperature of 250 to 350°F. The crude gases pass through a cyclone dust collector, to remove fine particles of fluorspar carried over, and thence to a scrubber. Here entrained sulfuric acid is removed by countercurrently flowing concentrated sulfuric acid. The acid flows into a bottom receiving tank and is recirculated and subsequently returned to the retort.

The gases, now reduced in temperature to about 150°F, are drawn into a series of absorption towers where virtually quantitative removal of hydrofluoric acid takes place. In the last absorber, the gases are drawn upwards against a spray of water by a vent fan which also exhausts unabsorbed gases from the system.

The absorption system, containing usually 7 towers (each 15 ft high) may be divided into so-called weak-acid (5 towers) and strong-acid (2 towers) absorbers. Approximately 10 per cent hydrofluoric acid leaves the last tower, from which it is pumped through a water cooler (Karbate coils) into the preceding tower, where it is concentrated further. By continuing this process the concentration increases, until the acid leaving the first of the weak-acid towers (all usually packed with carbon Raschig rings) is 50 to 52 per cent H_2F_2. This material may be withdrawn for sale or concentrated further by circulation through strong-acid absorbers (plate and ring-cascade type) and cooling to 20 to 40°F in a brine-refrigerated shell-and-tube exchanger. The acid discharged from the absorber contains 80 per cent H_2F_2 and is stored in mild-carbon-steel tanks, from which it may be withdrawn for sale or concentrated to anhydrous acid.

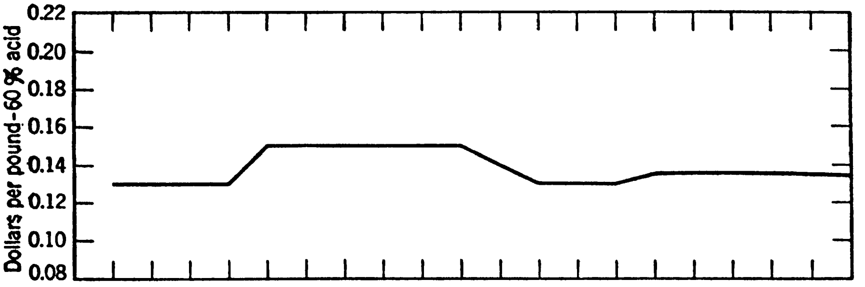
The 80 per cent acid from storage is pumped into a continuous fractionating column. Constructed of copper, the column is about 10 ft high and 3 ft in diameter and has a conventional kettle-type copper reboiler. At approximately 240°F stripping is carried out, with anhydrous acid leaving the top and about 40 per cent acid the bottom. The dilute acid is returned to the absorption system. The anhydrous gas is cooled to about 50°F in a steel shell-and-tube condenser chilled with "Freon"-refrigerated brine. The liquid anhydrous hydrofluoric acid is fed by gravity into insulated steel storage tanks for sale.



Production—Hydrofluoric Acid

Use Pattern

Alkylation	No breakdown available
Inorganic fluorides	
Sodium fluoride	
Antimony trifluoride	
Organic fluorine compounds	
Dichlorodifluoromethane	
Mixed chloro-, fluoro-derivatives of methane, ethane, and propane	
"Fluorcarbons" and their polymers	
Miscellaneous, including glass etching and enamel stripping	



Price—Hydrofluoric Acid

Miscellaneous

Properties. Anhydrous hydrofluoric acid is a colorless, fuming, corrosive liquid, which causes extremely serious burns on skin contact. Vapors are very irritating to the eyes and mucous membranes.

Mol. wt.	20.01	M.P.	−83°C
Sp. gr.	0.988 (13.6°C)	B.P.	19.4°C

Soluble in water in all proportions, in 100 per cent sulfuric acid (33 per cent at 30°C), benzene (2.25 per cent at 0°C), toluene (1.54 per cent at 0°C), anthracene (3.11 per cent at 0°C), xylene (1.01 per cent at 0°C), and tetralin (0.23 per cent at 0°C).

Aqueous hydrofluoric acid is available in standard commercial strengths of 30, 48, 52, and 60 per cent.

Acid strength, per cent	30	48	52	60
Sp. gr., at 0°C	1.119	1.188	1.205	1.235
F.P., °C	−69	−38.8	−35.2	−41.6
B.P., °C	109	106	101	85
Weight per gallon, lb at 0°C	9.34	9.91	10.06	10.31

Grades. Anhydrous (99 per cent minimum) and technical (aqueous solutions of 30, 48, 52, and 60 per cent acid).

Containers and Regulations. Anhydrous: steel tank cars and steel cylinders. Aqueous: 60 per cent—steel tank cars and drums; 30 to 52 per cent—rubber-lined drums and small plastic bottles; 30 per cent—rubber-lined drums, wooden barrels, and small plastic bottles. Some aqueous acid below 65 per cent strength is also shipped in lead carboys. Glass is attacked by hydrofluoric acid and cannot be used as a container. All grades of acid require a white ICC shipping label.

Economic Aspects

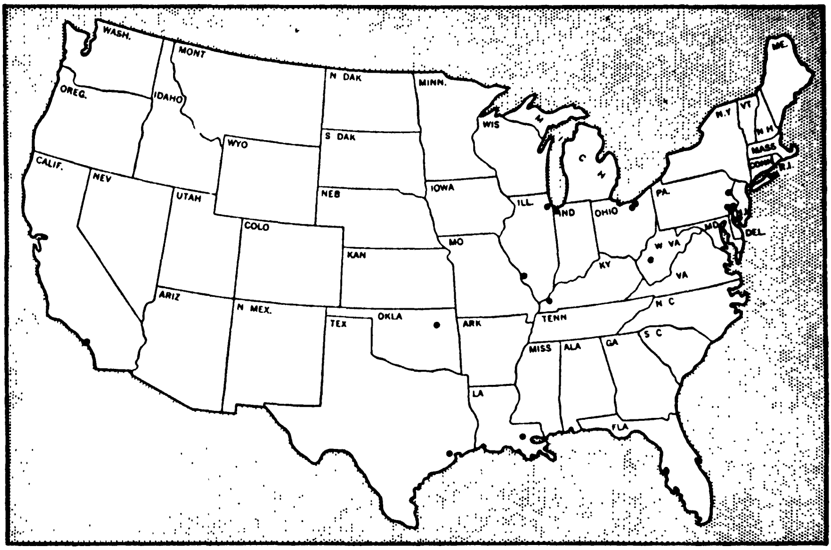
The war years saw a tremendous increase in the production and use of hydrofluoric acid. In general, the manufacturers of this acid also make a wide variety of other acids and heavy chemicals or a variety of fluorine derivatives.

Anhydrous hydrofluoric acid was produced first in 1931. Since then, demands for this grade for alkylation, "Freon-12," and military use have increased to a point where more than half the current acid capacity is for the anhydrous product. Chief competition will be in alkylation use where many refiners still prefer the sulfuric-acid alkylation process. Development of a suitable method for recovering sulfuric-acid sludge will only make competition between the two processes closer.

There is no doubt, however, that the availability of large quantities of hydrofluoric acid at a comparatively low price will engender wider use for a number of fluorine derivatives.

Plants normally vary in size from 100 to 700 tons annually. In this range plant cost will vary from $100 to $140 per annual ton capacity. Medium-size plants for hydrofluoric acid produce 200 to 600 tons annually, although one is known to have an annual capacity of 20,000 tons. The cost of a hydrofluoric-acid plant is determined largely by the method of utilization of weak acid from the bottom of the hydrofluoric-acid still.

Safety is an important item around a hydrofluoric-acid plant because of the extremely great hazards to personnel involved in handling it. Waste disposal also presents a specialized problem.

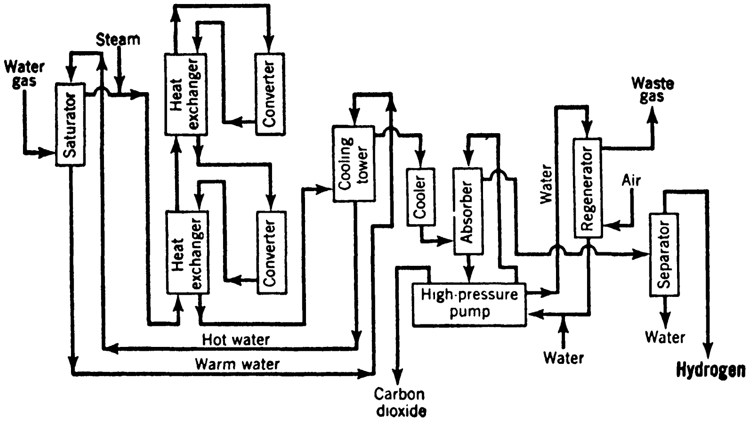


Location of Hydrofluoric-Acid Plants

HYDROGEN

H_2

From Water Gas and Steam



Reaction

$$C\ (\text{amorph}) + H_2O \rightarrow CO + H_2\ (\text{water gas})$$

$$CO + H_2O \rightarrow CO_2 + H_2$$

94–96% (conversion of CO)

Material and Utility Requirements

Basis—1,000 standard cu ft hydrogen (97%)

Coke	42 lb	Cooling water	2,000 gal
Steam	445 lb	Electricity	3 kw-hr

Process

Hydrogen is produced along with carbon dioxide by catalytically reacting water gas (40 per cent carbon monoxide–50 per cent hydrogen) with steam at elevated temperatures. The carbon dioxide is removed by scrubbing the gas; relatively pure hydrogen remains. At the present time this process accounts for the bulk of hydrogen produced in the United States and is particularly adaptable to low-purity hydrogen containing nitrogen and carbon monoxide for the synthesis of ammonia and methanol, respectively.

Water gas, also called blue gas, is produced by the reaction of steam on incandescent coke or coal at a temperature of 1,830°F or higher. Analysis of the gas approximates 40 per cent carbon monoxide, 50 per cent hydrogen, 5 per cent carbon dioxide, and 5 per cent nitrogen and methane. The gas from a holder is run into a saturator where it contacts hot water and is heated to 165 to 185°F. The saturated water gas (one volume) is then mixed with steam (three volumes) and passed into a two-stage catalytic converter, where carbon monoxide is reacted with water vapor. The first stage operates at a temperature of 800 to 900°F, and the second at 700 to 750°F with heat exchangers between the stages. Two stages are employed because of the exothermic character of the reaction and the decreased conversion at higher temperatures. By using this two-stage procedure on the so-called water-gas shift reaction, the major part of the conversion takes place with a relatively small amount of catalyst, whereas the balance is effected at a lower temperature conducive to high over-all yield. The catalyst commonly used is iron oxide promoted with chromium oxide and is required in amounts of 400 to 600 lb per 1,000 cu ft of water gas converted per hr. The life of the catalyst is long; it is ordinarily not necessary to remove sulfur compounds from the water gas because the catalyst is sulfur-resistant and converts sulfur compounds into hydrogen sulfide, which is removed with the carbon dioxide.

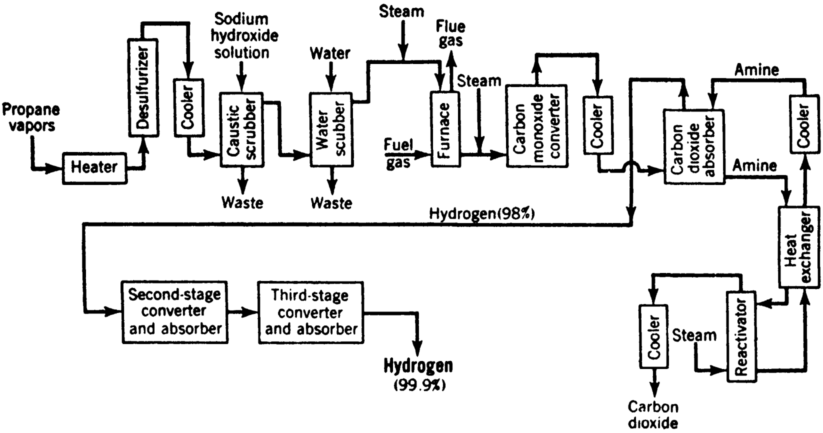
The exit gases, containing about 64 per cent hydrogen, 31 per cent carbon dioxide, 4 per cent nitrogen and methane, and 1 per cent carbon monoxide, are cooled in water towers and passed to purification units.

The method of purifying depends on the ultimate use of the hydrogen gas. For uses at high pressures, the reaction gases may be compressed to 200 to 400 psi and passed through water scrubbers where most of the carbon dioxide is removed. About a 3 to 5 per cent loss of hydrogen takes place because of its solubility at these pressures in water. The resulting gas contains 0.5 to 1.5 per cent residual carbon dioxide and 1.5 to 2.0 per cent carbon monoxide. These impurities may be removed by compressing the gas to 2,000 to 3,000 psi and scrubbing with an ammoniacal cuprous formate solution.

The gaseous mixture from the converters may be purified at atmospheric pressure by scrubbing with amine solutions. This method, known as the Girbotol process, saves compression costs and avoids hydrogen loss, owing to the water-scrubbing operation. After carbon dioxide removal by this method, the gases analyze about 97.2 mole per cent hydrogen, 1.2 per cent carbon monoxide, 1.2 per cent nitrogen, 0.3 per cent methane, and 0.1 per cent carbon dioxide. Purer hydrogen may be obtained by starting with a lower-nitrogen-content water gas and catalytically removing the carbon monoxide (see section on the iron–steam process). For details on the amine purification process, see the next section on the hydrocarbon–steam process.

The composition of the starting water gas is varied to suit the end use destined for the hydrogen. For ammonia synthesis, a semiwater gas is generated so that after conversion it contains the proper ratio of nitrogen to hydrogen (see *Ammonia* for details). A low-nitrogen water gas is produced for methanol synthesis, which requires a ratio of 2 moles hydrogen to 1 mole carbon monoxide in the starting gases (see *Methanol*).

From Hydrocarbons and Steam



Reaction

$$CH_3CH_2CH_3 + 3H_2O \rightarrow 3CO + 7H_2$$

$$3CO + 3H_2O \rightarrow 3CO_2 + 3H_2$$

$$CH_3CH_2CH_3 + 6H_2O \rightarrow 3CO_2 + 10H_2$$

Material and Utility Requirements

Basis—1,000 standard cu ft hydrogen (99.9%)

Propane	2.75 gal	Fuel (gas or oil)	350,000 Btu
(or natural gas	250 cu ft)	Cooling water	1,800 gal
Steam	360 lb	Electricity	2 kw-hr

Process

Large quantities of hydrogen are manufactured by catalytically reacting hydrocarbons and steam, to yield hydrogen and carbon oxides, followed by the water-gas shift reaction. Both natural and refinery gases may be used as raw materials.

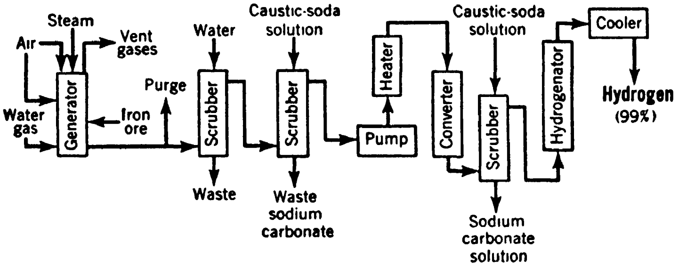
Commercial propane, obtained from either natural-gasoline plants or oil refineries, contains small amounts of organic sulfur compounds, which are removed before processing. The propane from storage passes in the form of vapors through a heater at a temperature of about 700°F. The hot gases then pass over a bauxite or metallic oxide catalyst, which converts the sulfur compounds (mercaptans, organic sulfides, and carbonyl sulfide) into hydrogen sulfide. After cooling, the gases are scrubbed with aqueous sodium hydroxide and water to remove the soluble sulfides.

The sulfur-free propane vapors are mixed with steam and passed into the top of a re-forming furnace. One type of furnace consists of a number of vertical nickel–chromium–iron alloy tubes, 3 to 8 in. in diameter and about 25 ft long, mounted in a refractory furnace. Heat for the endothermic reaction is supplied by multiple horizontal burners located at various levels with the flue gases passing upward countercurrent to the process gas. At temperatures of 1,400 to 1,800°F, the propane gas passes down the tubes over a supported nickel catalyst at a space velocity of about 600 volumes per hour per volume of catalyst. The propane is converted to hydrogen, carbon monoxide, and carbon dioxide, with a trace of methane remaining in the mixture.

These gases are cooled to about 700°F by mixing with steam and then passed into the first-stage carbon monoxide converter containing an iron oxide catalyst promoted with chromium oxide. Here the exothermic conversion reaction (water-gas shift) takes place at a temperature of about 800°F and a space velocity of 100 (or greater) volumes of gas per volume of catalyst per hour. Both this catalyst and the nickel-reforming catalyst are rugged and have a normal life of one year or more.

From the converter, the gases containing a small amount of carbon monoxide are cooled to about 100°F and passed into a packed (or bubble-tray) tower. Here aqueous 15 to 20 per cent monoethanolamine is circulated down through the countercurrently blowing gas (Girbotol process). The amine solution absorbs the carbon dioxide and, after passing through heat exchangers, is run to the top of a reactivating tower. Here the carbon dioxide is desorbed by steam generated by heating the solution in a reboiler at the bottom of the tower. The carbon dioxide removed amounts to about 300 cu ft per 1,000 cu ft of hydrogen, and, since it is recovered at a purity of 99.8 per cent, it is available as a useful by-product. The regenerated amine solution is then returned to the system. At atmospheric pressure and 100°F, hydrogen gas containing 20 per cent carbon dioxide may be purified to 0.1 per cent carbon dioxide by scrubbing, with the monoethanolamine absorbing 2 to 4 cu ft carbon dioxide per gal of solution circulated. Approximately 1 lb steam per gal of solution is required for regeneration. The carbon dioxide-free hydrogen coming from the absorber still contains about 1 per cent carbon monoxide. This is removed by passing through two more stages of carbon monoxide conversion, followed by carbon dioxide removal. From the last absorber, the purified hydrogen analyzes better than 99.9 per cent pure. The gas may be compressed to about 150 psi and charged into storage tanks.

From Iron and Steam



Reaction

Reducing phase:

$$2Fe_3O_4 + H_2 + CO \rightarrow 6FeO + CO_2 + H_2O$$

$$2FeO + H_2 + CO \rightarrow 2Fe + CO_2 + H_2O$$

Steaming phase:

$$Fe + H_2O \rightarrow FeO + H_2$$

$$3FeO + H_2O \rightarrow Fe_3O_4 + H_2$$

Material and Utility Requirements

Basis—1,000 standard cu ft hydrogen (99%)

Coke (to make water gas)	65–85 lb	Cooling water	1,000 gal
Steam	500–600 lb	Electricity	2 kw-hr
Fuel	30,000 Btu		

Process

Hydrogen is produced by the action of steam on iron ore, which has been previously reduced by treatment with a reducing gas such as water gas (40 per cent carbon monoxide–50 per cent hydrogen) or producer gas (25 per cent carbon monoxide–15 per cent hydrogen). This is one of the oldest commercial processes for hydrogen manufacture, and, although the total quantity of hydrogen manufactured in this manner is small compared to the previously described processes, there are a large number of plants in operation.

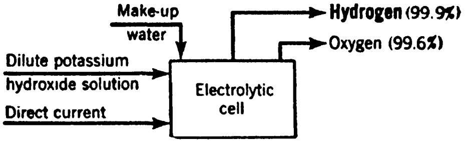
Various types of retorts have been used for the reaction including those of the Lane, Messerschmitt, and Bamag type. The last, also known as the shaft-type generator, consists of a cylindrical steel shell lined with refractory brick. It contains a bed of iron ore about 6 to 7 ft deep supported by a grate. The space above the ore bed is the combustion chamber, and above that is a chamber filled with refractory checkerwork which acts as the steam preheater. Side openings are provided for charging and discharging the ore.

Lumps of iron ore about 0.75 to 1.5 in. in diameter are charged into the retort. Here the ore is roasted to convert the iron carbonate to iron oxide. During this heating-up period, which may take several days, water gas or any other suitable fuel gas is burned. When operating temperatures of 1,500 to 1,800°F are reached, the cycle is started. Water gas (or another reducing gas) is admitted at the bottom of the retort and passes upwards through the porous iron oxide, reducing it to a mixture of ferrous oxide and metallic iron. The water gas is ignited above the ore bed by mixing with secondary air and serves to heat the checkerwork. The reducing gas is then turned off, and steam is introduced at the top and passes down through the checkerwork preheater and ore bed. The first hydrogen produced is purged to the atmosphere to remove residual reducing gas. At the end of the steaming cycle, air is passed down through the ore bed to burn off accumulated sulfur compounds and carbon. The sulfur results from its occurrence in the reducing gas, and, although a large part is converted to hydrogen sulfide during steaming, a certain amount remains. A normal operating cycle is 10 to 15 min, approximately equally divided between reducing and steaming with about 20 sec for purging and 20 sec for valve changing. Although about 1 ton of ore is required per 1,000 cu ft of hydrogen produced per hr, the efficiency of utilization is very small; only about 2 per cent of the ore is reduced and oxidized. Production of 1,500,000 to 3,000,000 cu ft of hydrogen per ton of ore is normally realized before it loses activity and must be replaced.

The crude hydrogen, which may contain 0.2 to 0.5 per cent carbon dioxide and 0.1 to 0.5 per cent hydrogen sulfide, produced during the steaming cycle, passes from the generator into a cooling tower where it meets countercurrently flowing water. It is then scrubbed with 10 per cent aqueous sodium hydroxide to remove the carbon dioxide and hydrogen sulfide. At this point the hydrogen is better than 98 per cent pure and contains about 0.3 per cent carbon monoxide.

The hydrogen may be further purified by mixing it with steam, heating to about 700°F, and passing the mixture over an activated, chromium-promoted iron oxide catalyst. The carbon monoxide is oxidized by the steam to carbon dioxide. After the gas mixture is cooled, it is again scrubbed with sodium hydroxide to remove carbon dioxide. Aqueous solutions of amines may also be utilized. The last traces of carbon monoxide may be removed by passing the gas over a nickel catalyst at 500 to 600°F. Here the carbon monoxide is hydrogenated to methane to give hydrogen of 99.0 to 99.7 per cent purity, depending on the amount of purging employed; the balance is nitrogen and methane. The purified hydrogen, after cooling, is stored in a gas holder.

From Water by Electrolysis



Reaction

$$4\text{KOH} \rightarrow 4\text{K}^+ + 4(\text{OH})^-$$

$$4\text{K}^+ + 4\text{H}_2\text{O} \rightarrow 4\text{KOH} + 2\text{H}_2$$

$$4(\text{OH})^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2$$

96–100% current efficiency

Material and Utility Requirements

Basis—1,000 standard cu ft hydrogen (99.9%)

Water (make-up)	6.5–7.0 gal
Electricity	140–160 kw-hr

Process

Although accounting for only a minor portion of the total hydrogen output, the electrolysis of water yields both high-purity hydrogen and oxygen. Solutions of potassium or sodium hydroxide in distilled water are usually employed because of the low electric conductivity of pure water. On passage of an electric current through the solution, the metal ions migrate to the negative electrode (cathode), where they combine with electrons to form atoms, which react with the water to regenerate the metallic hydroxide and produce hydrogen. Simultaneously, hydroxyl ions migrate to the positive electrode (anode), where they lose electrons and combine to form water molecules and oxygen atoms; the latter combine to produce oxygen molecules. The solution is circulated through the cell to prevent concentration of the caustic at the cathode, and the gases pass separately to chambers above the respective electrodes.

Two general types of cells are used for the electrolysis of water: the unipolar cell (both open and closed tanks) and the bipolar or filter-press cell. The latter is used principally in Europe.

In the unipolar or tank-type cell, large parallel electrodes are suspended in a tank of electrolyte. A typical closed tank cell contains 15 electrodes (7 anodes and 8 cathodes), each about 39 in. square and spaced about 1.3 in. apart. An odd number of electrodes is employed to maintain the steel tank at a uniform potential on both sides. Alternate electrodes are connected in parallel, and the cells are connected in series to a source of direct current: for example, mercury-arc rectifiers. The cathodes are made of iron and the anodes usually of nickel-plated (0.003 in.) iron. Between the electrodes are diaphragms, which prevent the mixing of hydrogen and oxygen gas but allow the passage of the electrolyte. The diaphragms are usually made of asbestos cloth, although perforated nickel plates or wire screens may be used. The top of the cell is constructed of reinforced concrete, and the tank is mild steel.

Distilled water and either potassium or sodium hydroxide are charged into the cells. With potassium hydroxide, a 34 weight per cent solution is made up, whereas with sodium hydroxide the concentration is about 25 per cent. At these concentrations the maximum conductivity is obtained at 167°F. Since the conductivity increases with temperature, 167°F represents the practical operating temperature without promoting evolution of excessive amounts of water vapor. The heat liberated by electrolysis raises the cells to the operating temperature, which is then maintained by external cooling with running water.

Direct current, produced by rectification of alternating current (rectifier efficiency about 90 per cent), flows into the cells at 10,000 amperes. Normal operating current density is 67 amperes per square foot of electrode. The cell voltage is about 2.25, which represents an overvoltage of 1.02 volts; the theoretical voltage required to dissociate water is 1.23 volts. The current efficiency (ratio of amount of hydrogen and oxygen actually produced to the theoretical amount liberated by unit quantity of electricity) is 96 to 100 per cent. Make-up distilled water, from 6.5 to 8 gal per 1,000 cu ft hydrogen, is added automatically. Since no electrolyte is consumed in the process, only a small amount is added from time to time to make up for mechanical losses and contamination.

At substantially atmospheric pressure (4 in. water column), 99.6 per cent oxygen is generated at the anode and passes into the collecting chamber above the electrode. At the cathode, 99.9 per cent hydrogen is obtained at a rate of about 7 cu ft per kw-hr. This high-purity hydrogen contains only traces of oxygen which, for special applications, may be removed by passage over catalysts at elevated temperatures. The gases may be used directly or compressed for filling into cylinders.

Hydrogen is also obtained as a by-product in other electrochemical processes. Typical examples are the electrolysis of sodium chloride solutions for the manufacture of chlorine, sodium hydroxide, sodium chlorate, and sodium perchlorate. For details, see *Chlorine*, *Sodium Hydroxide*, and *Sodium Chlorate.*

Thermal Decomposition of Hydrocarbons

Hydrogen is obtained as a by-product in the manufacture of carbon black by the thermal decomposition of natural gas. A brick checkerwork chamber is heated to 2,000 to 2,500°F, and natural gas is passed through. After the carbon black is separated, the gases contain 70 to 85 per cent hydrogen. By scrubbing to remove carbon oxides, hydrogen pure enough for ammonia synthesis is obtained. This process is one of the cheapest sources of low-purity hydrogen. For details on furnace operations, see *Carbon Black.*

From Methanol and Steam

Hydrogen of higher than 98 per cent purity may be manufactured by the catalytic reaction of methanol and steam at 500°F, according to the following equation:

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$$

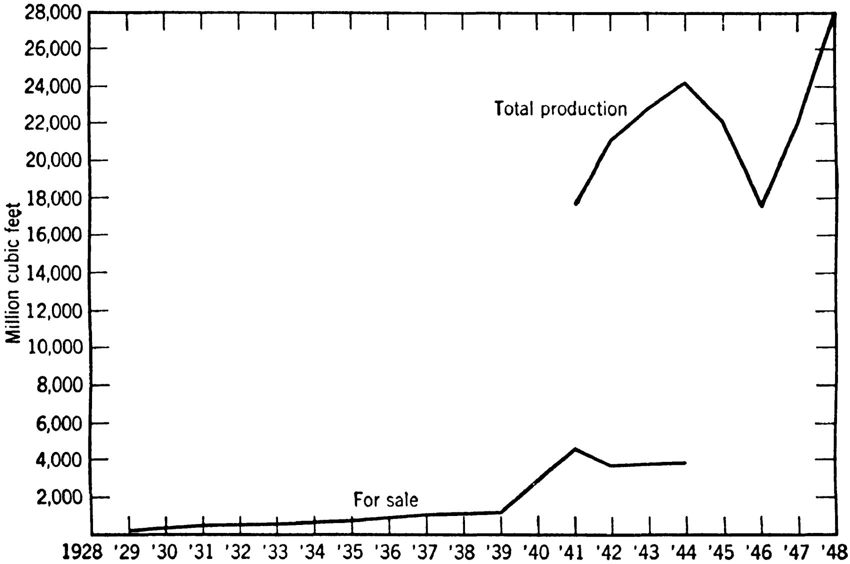
The exothermic reaction at moderately low temperatures may be conducted at up to 300 psi so that the hydrogen can be delivered at elevated pressures. For 1,000 standard cubic feet of hydrogen plus 39 lb of pure by-product carbon dioxide, approximately 5 gal of methanol and 4 gal of fuel are required. The ease and simplicity of fabricating the plant, handling raw materials, and purifying the hydrogen make this process particularly practical for portable plants. The present cost of methanol as a raw material, of course, precludes the widespread or large-scale use of this process.

From Ammonia by Dissociation

For metal treating and hydrogen welding, a source of mixed gas (75 per cent hydrogen–25 per cent nitrogen) is the catalytic cracking of ammonia. Economies in transportation and storage make this process feasible for small-scale usage in special applications. Since each pound of liquid ammonia yields 45 cu ft of dissociated gas containing approximately 34 cu ft of hydrogen and 11 cu ft of nitrogen, it is claimed that a single 150-lb cylinder of liquid ammonia can replace 33 cylinders of hydrogen. Pure nitrogen may also be obtained by burning out the hydrogen at a cost comparable to or perhaps lower than cylinder nitrogen. It is not economically feasible, however, to produce pure hydrogen by this process.

Other Processes

Hydrogen is also obtained as a by-product from butanol fermentation (see *Acetone, Butyl Alcohol*) and dehydrogenation of materials such as butane (for the manufacture of butadiene) and methyl cyclohexane (for the production of toluene). Liquefaction processes for the separation of hydrogen from coke-oven gas and water gas have also been used in Europe but have not been utilized to any extent in the United States.



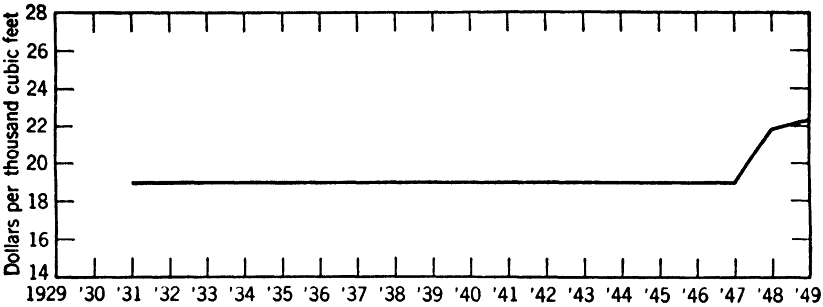
Production—Hydrogen

Use Pattern

Production figures for hydrogen obviously do not include water gas and similar impure streams. Accordingly, a use pattern cannot be correlated with production data.

The hydrogen requirements for various end uses are:

Ammonia (synthetic)	84,000 cu ft per ton
Methanol (synthetic)	225 cu ft per gal
Iso-octane	1,600 cu ft per bbl
Hardened vegetable oils	1,500 cu ft per ton
Cyclohexanol	25,000 cu ft per ton



Price—Hydrogen (Cylinders, Open Market)

Miscellaneous

Properties. Colorless, highly flammable gas.

Mol. wt.	2.016	M.P.	−259.1°C
Sp. gr.		B.P.	−252.8°C
Gas	0.06948 (air = 1)		
Liquid	0.0709 (−252.7°C)		

Soluble in water (2.1 cc per 100 g at 0°C, 0.85 cc per 100 g at 80°C). Slightly soluble in iron, palladium, and platinum.

Flash point (closed cup)	Gas
Ignition temperature	1,085°F
Vapor density (air = 1)	0.069
Explosive limits (% by volume in air)	Lower 4.1 Upper 74.2

Grades. Technical and pure.

Containers and Regulations. Steel cylinders. Red (gas) ICC shipping label required.

Economic Aspects

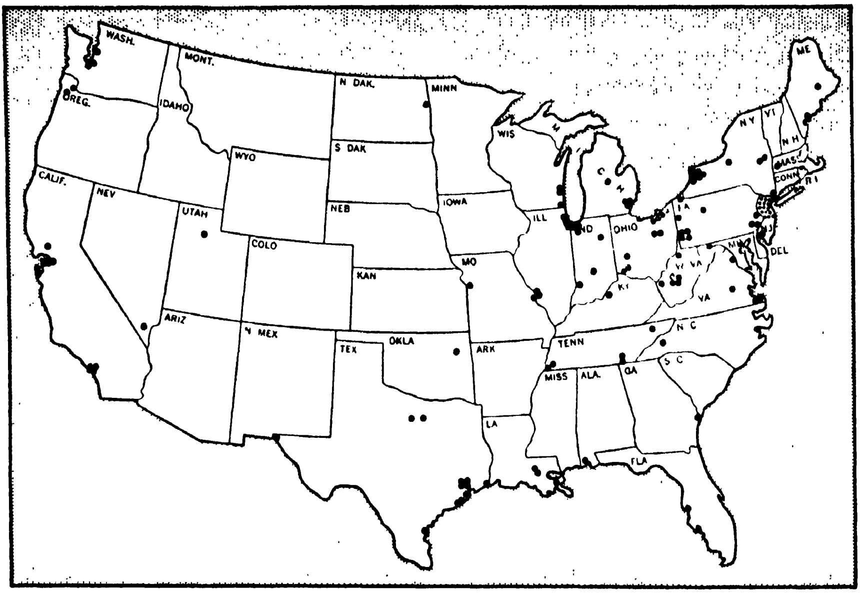
The manufacture of hydrogen is unique in that there are so many highly competitive processes by which it can be made. Contributing factors to competition among the various processes are (1) variations in productive capacity desired and (2) wide variations in purity desired. Of the total United States production, approximately 50 per cent is used in the making of synthetic ammonia. In this case, synthesis gas containing a ratio of 3 moles of hydrogen to 1 mole of nitrogen is desired, with the result that in many cases no attempt is made to separate the two gases. A similar operation of great potential importance is the production of synthesis gas for the Fischer–Tropsch process. A 25,000-bbl-per-day plant will require over 700,000,000 cu ft of synthesis gas (hydrogen and carbon monoxide) per day. Purity requirements for other hydrogenation processes may vary from 97 per cent to nearly 100 per cent pure hydrogen.

The most important processes from the standpoint of both productive capacity and total number of plants are the steam–iron, steam–water-gas, steam–hydrocarbon and electrolytic processes. Greatest production is by the steam–water-gas process with the steam–hydrocarbon process in second place. The percentage of total production made in electrolytic plants and by the steam–iron process is not great, but many small and medium-size plants for both processes are in operation.

In the past, only electrolytic plants were used for the production of less than 5,000 cu ft hydrogen per hr, but steam–hydrocarbon plants are now being adapted to plants with capacities as low as 1,000 cu ft per hr. Steam–iron and steam–hydrocarbon processes are directly competitive in the range of 5,000 to 15,000 cu ft per hr. The investment required for the steam–hydrocarbon process in this range is slightly more than for the steam–iron process, but this cost is offset by lower operating costs. Above 15,000 cu ft per hr, the steam–iron, steam–hydrocarbon, and steam–water-gas processes are all used, with the choice dependent on relative costs of raw materials and purity of hydrogen desired. Before World War II, only two synthetic-ammonia plants used the steam–hydrocarbon process, but during the war six of ten new ammonia plants built adopted the process. Hydrogen purity of 99.97 per cent has been obtained in a propane–steam process.

Various minor hydrogen processes in use include (1) thermal decomposition of hydrocarbons (one plant), (2) steam–methanol process (used in portable military plants during World War II), (3) recovery from coke-oven gas by liquefaction (used largely in Europe), (4) cracking of ammonia (suitable for heat treating of metals), and (5) by-product hydrogen (from alkali–chlorine cells, acetone–butanol fermentation gases, and dehydrogenation processes, such as the conversion of butane to butadiene). Some use was also made during the war of the caustic-soda–ferrosilicon process and the hydrolysis of sodium borohydride, but the steam–methanol process mentioned previously was far more important. Portable plants using this process had capacities of 4,000 cu ft hydrogen and 15 lb carbon dioxide per hr.

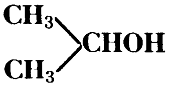
Since the war, many hydrogen users, principally alloy-steel fabricators, have found it cheaper to buy ammonia and crack it to hydrogen and nitrogen, rather than make hydrogen by other means. The possibilities for expansion of this practice appear very bright.



Location of Hydrogen Plants

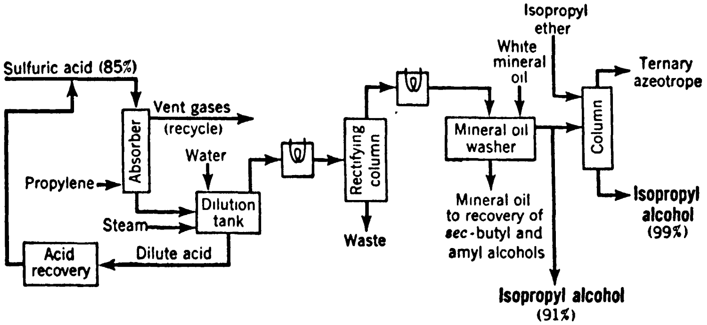
ISOPROPYL ALCOHOL

(PROPANOL-2)



$$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>CHOH$$

From Propylene



Reaction

$$CH_3CH = CH_2 + H_2SO_4 \rightarrow CH_3CH(OSO_3H)CH_3$$

$$CH_3CH(OSO_3H)CH_3 + H_2O \rightarrow CH_3CH(OH)CH_3 + H_2SO_4$$

70% yield

Material Requirements

Basis—1 ton isopropyl alcohol (91%)

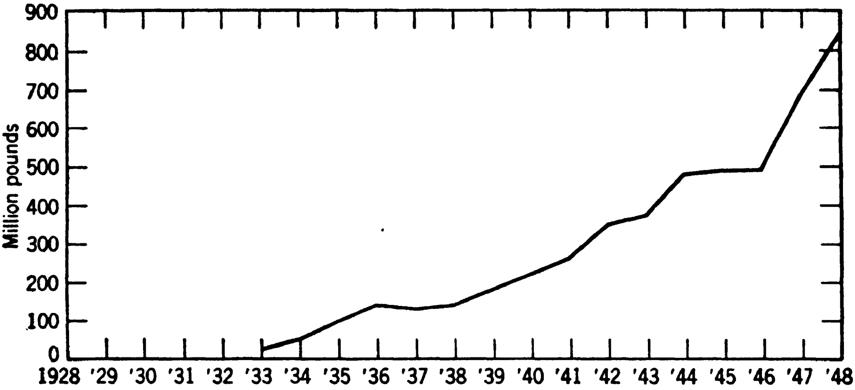
Propylene	1,800 lb
Sulfuric acid (85%)	25 lb
Mineral oil	Losses only

Process

Propylene is absorbed by sulfuric acid to form propyl sulfate, which is subsequently hydrolyzed with water to isopropyl alcohol and dilute sulfuric acid.

Cracking still gases, rich in propylene, are desulfurized and passed into the bottom of a packed absorption tower maintained at 21 to 27°C.

Sulfuric acid (85 per cent) is introduced into the top of the absorber and passes countercurrent to the propylene gases. The reaction is strongly exothermic and necessitates cooling the tower with brine to prevent a temperature rise. Approximately 50 per cent of the propylene is absorbed to form mostly isopropyl-acid sulfate and some diisopropyl sulfate. Essentially no ethylene is absorbed at 24 to 27°C, using 85 per cent sulfuric acid; it passes through the vent with unabsorbed propylene. The gases are recycled until the ethylene content rises too high. The ethylene may then be used to produce ethyl alcohol (see *Ethyl Alcohol*).



Production—Isopropyl Alcohol (100%)

The higher olefins such as butylene or amylene that may be present are absorbed along with the propylene.

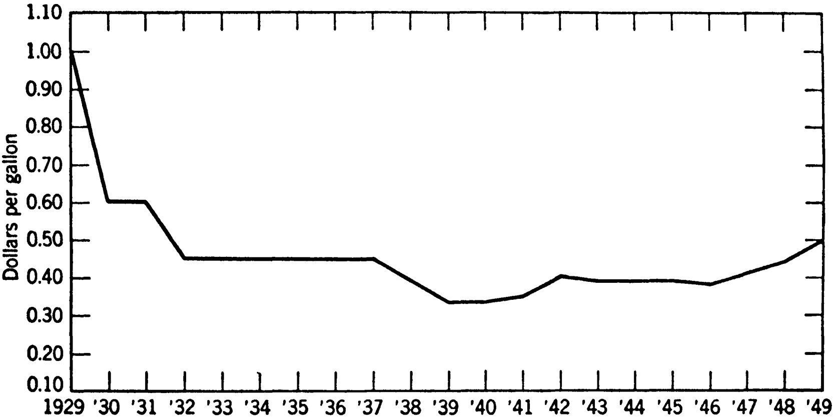
The reaction mixture is withdrawn from the base of the tower and charged into a closed lead-lined dilution tank. Two to three volumes of water or steam are added so that a 20 per cent concentration results. The isopropyl sulfates are hydrolyzed to sulfuric acid and alcohol. The heat of dilution warms the mixture, and with the aid of additional steam the crude alcohol is driven off. The diluted sulfuric acid (about 1.4 sp. gr.) is concentrated to specific gravity of 1.8 and returned to the absorber. Eventually the acid is run to waste because of the gradual accumulation of tarry materials.

The crude alcohol is passed to a rectifying column for concentration. The 91 per cent isopropyl alcohol–water azeotrope distils from the top of the column and after cooling is passed through a mineral-oil washer. The mineral oil selectively absorbs any higher alcohols present such as secondary butyl alcohol (from butylene) and secondary amyl alcohol (from amylene). The resulting 91 per cent isopropyl alcohol is generally further purified by chlorine or sodium hypochlorite to yield the water-white technical-grade product. Absolute isopropyl alcohol (99 per cent) is obtained by distilling 91 per cent alcohol in the presence of diisopropyl ether. A ternary azeotrope of isopropyl ether (91.1 parts), isopropyl alcohol (5.8 parts), and water (3.1 parts), which boils at 61.4°C, is removed as overhead. Absolute isopropyl alcohol (99 per cent) leaves the bottom of the still. The azeotrope is washed with water, and the various components are recovered.

Normal propyl alcohol is not obtained in this process. Small amounts have heretofore been obtained from fusel oil (see *Amyl Alcohol* and *Ethyl Alcohol*). Greater amounts are now available as one of the products of aliphatic hydrocarbon oxidation (see *Acetaldehyde*).

Use Pattern

	1947 (est.), per cent
Acetone	70
Antifreeze	10
Other	20
	100



Price—Isopropyl Alcohol (91%)

Miscellaneous

Properties. *Propyl Alcohol, iso-*, $(CH_3)_2CHOH$. Colorless, flammable, mobile liquid.

Mol. wt.	60.09	M.P.	−89.5°C
Sp. gr.	0.789 20°C/4	B.P.	82.5°C

Weight per gallon 6.55 lb (20°C)

Soluble in water, alcohol, and ether.

Flash point (closed cup)	53°F
Ignition temperature	750°F
Vapor density (air = 1)	2.07
Explosive limits (% by volume in air)	Lower 2.5

Grades. 99 per cent and 91 per cent (88 per cent by weight).

Containers and Regulations. Tank cars, drums, and tins. Red ICC shipping label required.

Properties. *Propyl Alcohol, n-*, ($CH_3CH_2CH_2OH$). Colorless liquid with an odor similar to ethyl alcohol.

Mol. wt.	60.09	M.P.	−127°C
Sp. gr.	0.804 20°C/4	B.P.	97.8°C

Weight per gallon 6.7 lb. (20°C)

Soluble in water, alcohol, and ether.

Flash point (closed cup)	59°F
Ignition temperature	700°F
Vapor density (air = 1)	2.07
Explosive limits (% by volume in air)	Lower 2.15 Upper 13.5

Grades. Technical.

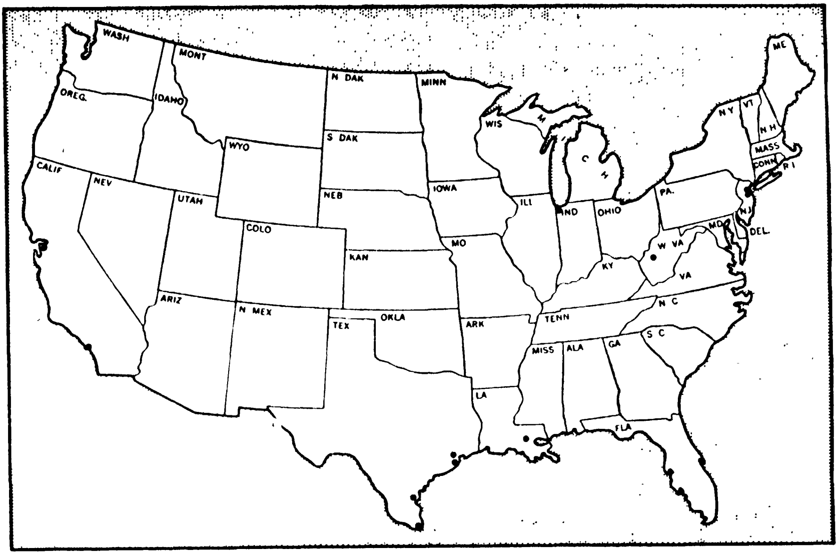
Containers and Regulations. Tank cars, drums, and bottles. Red ICC shipping label required.

Economic Aspects

The development of the manufacture of isopropyl alcohol by hydration of the olefin, propylene, parallels very closely the manufacture of synthetic ethyl alcohol, except that no large competitive process exists. A small amount of isopropyl alcohol may be recovered from fusel oil but is not so produced in a pure form. A recent patent describes a fermentation process for producing isopropyl alcohol as a by-product of butanol production (see *Butyl Alcohol*). Actually, the manufacture of isopropyl alcohol may be considered competitive with that of ethyl alcohol, since practically all the uses of the former were at one time supplied by ethyl alcohol.

The distinct advantage of isopropyl alcohol for many users is that it is tax-free and therefore not under Government regulation. It may not, however, be used in foods. Nevertheless, on a tonnage basis, isopropyl alcohol was the most important pure synthetic organic chemical just before and in the early part of World War II. Toward the end of the war butadiene production took first place.

For economic production, plants should have a capacity of at least 5,000,000 gal per yr. One plant of 20,000,000-gal capacity is known. A 10,000,000-gal plant would cost about $200,000 per 1,000,000 gal annual production.

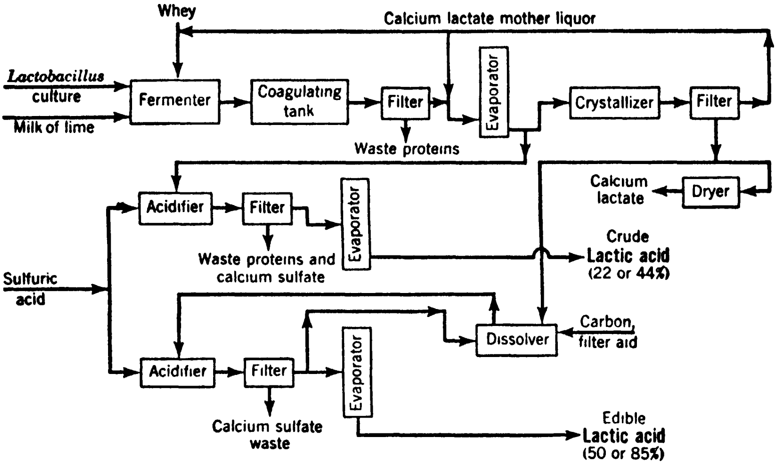


Location of Isopropyl Alcohol Plants

LACTIC ACID

$CH_3CHOHCOOH$

From Whey by Fermentation



Reaction

$$\underset{\text{Lactose (or sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Galactose (or fructose)}}{C_6H_{12}O_6}$$

$$C_6H_{12}O_6 \xrightarrow{\text{Bacteria}} 2CH_3CHOHCOOH$$

80–85% yield

Material Requirements

Basis—1 ton lactic acid (100%)

Whey	50,000 lb
Lime (hydrated)	2,000 lb
Sulfuric acid (100%)	1,160 lb

Process

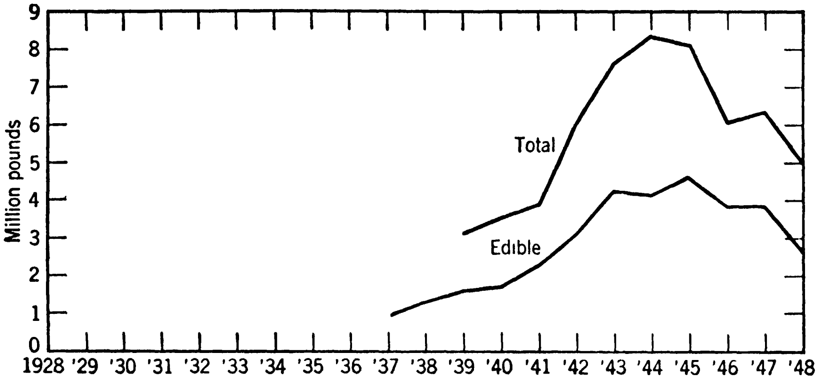
Lactic acid is produced by the controlled fermentation of various carbohydrates such as sucrose, glucose, or lactose. These sugars are obtained from molasses, corn or potato-starch hydrolyzates, and milk whey. Various fermentation bacteria are used, and the type depends on the raw materials utilized. *Lactobacillus delbrücki* is one of the most widely used when molasses or starch hydrolyzates serve as the raw material. However, this bacteria is not satisfactory for the fermentation of lactose (milk sugar). Regardless of the raw material used, the fermentations differ only in detail rather than in principle. The recovery of the lactic acid from the ferment medium is analogous in most cases.

Whey, a by-product in the manufacture of cheese from whole milk and casein from skim milk, is charged into a fermenter. It is inoculated with a culture of *Lactobacillus bulgaricus* grown in a laboratory on a culture medium of pasteurized skim milk. The fermenter is maintained at a temperature of about 110°F by means of steam coils. The *p*H of the medium during fermentation is held between 5.0 and 5.8. After 8 to 12 hr the *p*H drops to about 5.0. Small quantities of calcium hydroxide or carbonate are added at intervals to maintain the *p*H (acid concentration must be kept below 1.3 per cent for proper growth). The mixture is allowed to ferment 5 to 6 days until the optimum yield of lactic acid is obtained.

At the end of the fermentation, a slight excess of calcium hydroxide is added to bring the lactic acid wholly into the form of the salt: calcium lactate. The batch is run from the fermenter to a coagulating tank, where it is heated by steam to 190°F. Impurities such as lactalbumin are coagulated and after settling are filtered off. The calcium lactate mother liquor may be purified with decolorizing charcoal and concentrated in a vacuum evaporator. Part of the concentrated calcium lactate solution is allowed to crystallize. After filtration, the crystals are dried in pans to yield calcium lactate for sale. The mother liquor from the filtration is reintroduced into the system by part of it being added to the evaporator and the remaining part to the whey raw-material charge.

The remainder of the concentrated calcium lactate solution from the evaporator is acidified with dilute sulfuric acid, filtered to remove proteins and calcium sulfate (waste), and evaporated under vacuum to yield technical lactic acid. This solution is dark colored, contains certain organic impurities (from the original lactose), and generally assays 22 per cent lactic acid. Technical, 44 per cent lactic-acid solution may be obtained by further evaporation. These crude acids may be purified by various methods, such as extraction of the acid, using isopropyl ether as solvent, or by esterification with methanol, followed by hydrolysis to yield purified lactic acid.

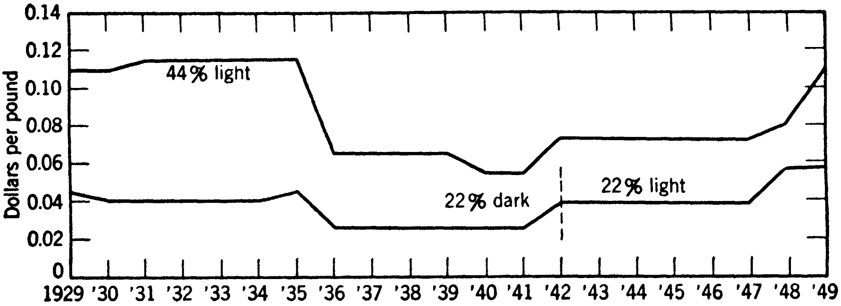
Edible lactic acid is generally obtained by dissolving the calcium lactate crystals from the filter (before drying) in water. This solution is acidulated with dilute sulfuric acid to give a 22 to 25 per cent purified lactic-acid solution. This acid is concentrated to 50 per cent acid by the addition of calcium lactate. Small amounts of activated charcoal and filter aid may be added. The lactic-acid–calcium lactate solution from the dissolver is run to an acidifier where sulfuric acid is added. The precipitated calcium sulfate (dihydrate) is filtered off and run to waste. The filtrate, purified lactic acid of 50 per cent concentration, is either packaged or concentrated by vacuum in stainless-steel evaporators to yield 85 per cent edible lactic-acid solution. The yield of lactic acid based on the lactose content of the whey is 80 to 85 per cent.



Production—Lactic Acid (100%)

Use Pattern

	1947 (est.), per cent
Food and beverages	30
Leather processing	30
Miscellaneous	40
	100



Price—Lactic Acid

Miscellaneous

Properties. Lactic acid, because of its optical activity, occurs in the dextro, levo, and racemic forms. The commercial acid is the racemic or inactive form which is a colorless or yellowish viscous liquid at normal temperatures.

Mol. wt.	90.08	M.P.	16.8°C
Sp. gr.	1.249 15°C/4	B.P.	122 (14 mm)°C

Soluble in water, alcohol, and ether, in all proportions.

Grades. Technical (22, 44, 66, and 80 per cent), edible (50 and 80 per cent), plastic (50 and 80 per cent), USP (75 and 85 per cent), and dilute (15 per cent).

Containers and Regulations. Tank cars, barrels, carboys, and bottles. No ICC shipping label required.

Economic Aspects

Since lactic acid may be manufactured with equal ease from molasses, glucose, or whey, the particular raw material used industrially depends largely on the raw-material sources of the producer. A strong raw-material position determines to a considerable extent whether or not a given manufacturer can enter the field economically.

As with most fermentation processes, adequate technology is a necessity, and so most manufacturers are at least subsidiaries of the larger companies. A considerable portion of the acid is now used for deliming in tannery operations, but competition from the cheaper glycolic acid may be expected. Further entrance of lactic acid into the food field appears inevitable. This depends somewhat on finding a suitable method for the manufacture of 100 per cent acid from the crude.

A much more recent use is as a plasticizer and catalyst in the casting of phenol–aldehyde resins. Indications are that this use may increase markedly in the future. On the other hand, if the price of lactic acid could be reduced markedly, there is little doubt but that its use as a chemical intermediate also would be expanded.

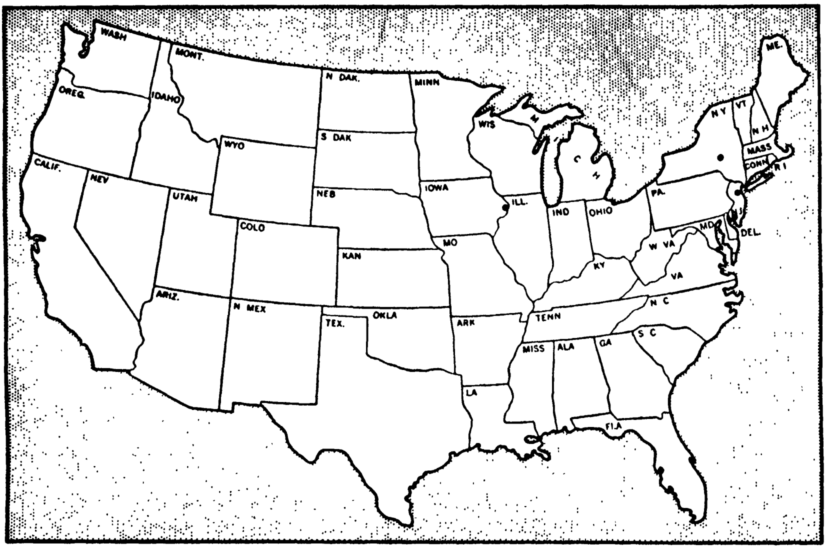
The chief manufacturing problems at present are corrosion difficulties and purification of the crude acid. All common cheap metals are attacked by lactic acid, and, although the high chrome–nickel steels show fairly good resistance, a satisfactory solution is not yet known.

Of the various methods of purification, that is, recrystallization of calcium lactate or zinc lactate, solvent extraction, and esterification with methanol, the last-named appears simplest at present.

A mold process has been developed, though not presently used, for the manufacture of *d*-lactic acid, in contrast to *d-l* lactic acid produced by conventional processes.

Alternate possible manufacturing processes for lactic acid, besides the process described, are hydrolysis of lactonitrile derived from acetaldehyde and hydrogen cyanide, and recovery of lactic acid present in corn steep liquor. Both processes are interesting and constitute threats to present processes but have not yet been proved feasible.

The range of fermentation plant sizes runs from 300 to 3,000 tons per year. A plant of the latter size requires an investment of approximately $1,000,000.



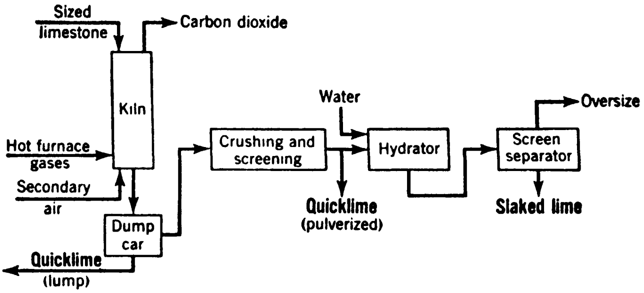
Location of Lactic-Acid Plants

LIME

(CALCIUM OXIDE)

CaO

From Limestone by Calcination



Reaction

$$CaCO_3 \rightarrow CaO + CO_2 \qquad \text{(Calcining)}$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad \text{(Hydrating)}$$

Material Requirements

Basis—1 ton quicklime (CaO)

Limestone (pure)	3,750 lb
Coal (bituminous)	650 lb

Process

Lime is produced by burning (calcining) various types of limestone in continuous vertical or rotary kilns.

Limestone (calcium carbonate, $CaCO_3$) is mined or quarried and is transported to the mills where it is crushed and screened. The sized limestone is then burned in continuous pot kilns, shaft kilns, or rotary kilns. For the burning of lump limestone (4 to 8 in.), vertical pot or shaft kilns are almost universally employed. Pot kilns differ from shaft kilns in that the stone and fuel (coal or coke) are added in alternate layers. These kilns are not favored, because they are restricted to solid fuels having enough strength to support the charge; such fuels produce ash, which contaminates the product.

Rotary kilns are particularly suitable for stone too fine (0.5 to 1.5 in.) to be burned in shaft kilns. The kiln consists of a firebrick-lined steel cylinder resting on heavy rings, which bear on steel rollers. It inclines slightly (0.5 in. per ft) and revolves slowly on its axis. Such a kiln will calcine up to 200 tons of lime in 24 hr and requires a heating time of about 3 hr per charge.

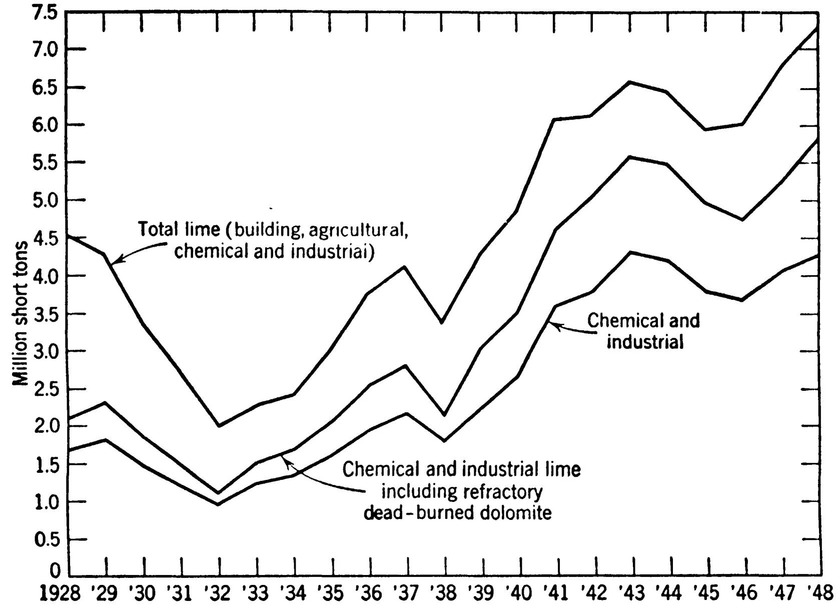
The shaft kiln consists of a short, wide stack, lined with a refractory material (firebrick). The outside construction is sheet steel for strength and prevention of gas leakage. In many cases the gases are allowed to escape from the top of the stack. If the carbon dioxide is to be recovered, the top of the kiln is closed, and the gases are conducted through a pipe under slight vacuum to compressors.

In shaft-kiln operation the limestone is conveyed to the top of the kiln where it is dumped into a hopper. Here it is preheated slowly by the hot kiln gases. The stone gradually slides down the shaft into the calcining zone. This section of the kiln is heated to a temperature of 1,000 to 1,100°C (calcium carbonate dissociates at 898°C, liberating carbon dioxide) by combustion gases from a firebox (coal grates or gas burners) arranged alongside the kiln. Coal or coke is the main fuel, although oil and gas may also be used. The fuel efficiency, using bituminous coal, is about 3.23 lb of lime per lb of coal (direct-fired) and 4.08 lb lime per lb of coal employing producer gas in shaft kilns. Rotary kilns require 1 lb coal to produce 3.37 lb lime.

The resulting lime from the hot zone sinks downward into the third section or cooler. The cooler generally contains ducts through which the air, used in burning the fuel, is drawn. This preheats the air and partially cools the hot lime. The doors are opened at intervals, permitting the cooled lime to fall into large iron barrows or dump cars. After further cooling, the lime is either packaged as lump lime or crushed and screened to yield pulverized lime. Containers that are air- and moisture-proof are preferred, since quicklime readily air-slakes.

Quicklime, crushed to 1 in. or smaller, is converted to the hydroxide (hydrated lime) in either intermittent or continuous hydrators. Lime and water are thoroughly mixed, resulting in the evolution of steam (the reaction is exothermic). When steam evolution has ceased, the hydration is complete, and the light, dry, slaked lime is discharged from the hydrators. It is then classified by screens or air separators, which remove any cores or overburned lime that did not hydrate. The finished slaked lime is stored in dustproof bins for aging and is generally packed in bags for shipment.

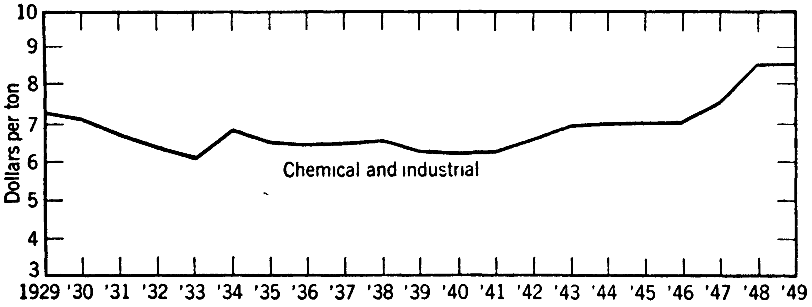
The amount of water required for slaking varies with the purity of the lime. However, 56 lb of quicklime (calcium oxide) requires 18 lb of water to produce 74 lb of the hydrate. The type of hydrator used varies from plant to plant. The intermittent type consists of a circular iron pan of about 1.5 tons capacity which horizontally revolves around a shaft. Arms carrying plows extend from the shaft, and agitation is obtained by the rotation of the pan. The continuous hydrator consists of a series of tubes, each containing a screw conveyer, through which the reactants (lime and water) are carried and thoroughly mixed. The dry product (slaked lime) is continuously discharged from the end of the tube.



Production—Lime

Use Pattern

	1946 (from Bureau of Mines Statistics), per cent
Total Lime	
Agriculture	6.4
Building	14.1
Chemical and industrial	61.5
Refractory	18.0
	100
Chemical and Industrial Lime	
Calcium carbide and cyanamid	10.3
Glass works	6.7
Insecticides and disinfectants	2.6
Metallurgy (steel flux and ore concentration)	29.3
Paper mills	15.4
Water purification	11.7
Tanneries	2.2
Miscellaneous	21.8
	100



Price—Lime

Miscellaneous

Properties. Colorless cubic crystals in the form of white hard lumps, which gradually crumble on exposure to air.

Mol. wt.	56.08	M.P.	2,570°C
Sp. gr.	3.32	B.P.	2,850°C

Soluble in water (forming calcium hydroxide, $Ca(OH)_2$, and generating a large quantity of heat) and acids. Insoluble in alcohol.

Calcium hydroxide (slaked lime): White, dry powder.

Mol. wt.	74.10	M.P.	Loses H_2O 580°C
Sp. gr.	2.2		

Soluble in ammonium chloride solution. Very slightly soluble in water (0.18 per cent at 0°C, 0.08 per cent at 100°C).

Grades. Quicklime: high-calcium lime (90 per cent calcium oxide), low-magnesium lime (5 to 25 per cent magnesia), dolomitic lime (25 to 45 per cent magnesia); hydraulic lime and slaked lime in various grades to meet the specifications of the agricultural, building, chemical, and industrial fields.

Containers and Regulations. Freight cars, wooden barrels, bags, kegs, cans, and bottles. No ICC shipping label required.

Economic Aspects

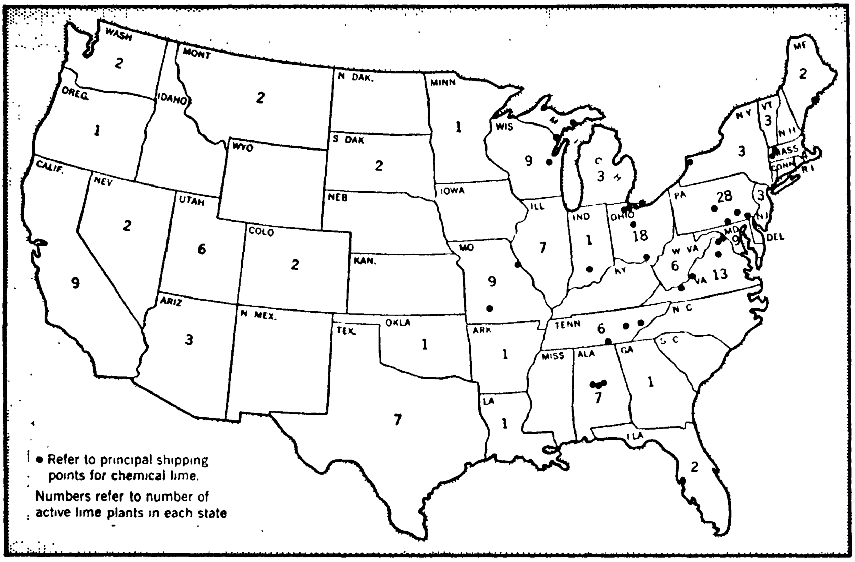
The burning of limestone to produce quicklime is one of the oldest chemical-manufacturing operations in America, as witnessed by the primitive lime kilns still standing in the eastern part of the United States. Some are still operated by local farmers.

Modern kilns are either of the vertical-shaft or rotary types, the former operated with either mixed or unmixed feeds. The ammonia-soda industry is the largest single consumer of lime. The industry operates its own kilns and recovers the carbon dioxide evolved, as well as the lime. Kilns are usually of the mixed-feed vertical-shaft type, since this type of kiln best lends itself to heat economy, high concentrations of carbon dioxide, and close chemical control.

Building lime manufacturers usually employ separate feed vertical kilns for operations producing less than 100 tons of lime per day, because of low ash contamination of the lime. For operations above 100 tons per day, rotary kilns are used. The largest rotary kilns have capacities as high as 250 tons per day. Such kilns are 500 ft long and 12 ft in diameter. In the ammonia-soda industry, however, modern vertical-shaft kilns have capacities as high as 300 tons of lime per day. Recent installations of inclined kilns are said, however, to have advantages over both rotary and vertical kilns. One of the most recent kiln installations (a 100-ton-per-day unit) utilizes a fluidization technique similar to that of the fluid cracking of petroleum.

Chemical lime is usually produced in rotary kilns, even in smaller operations, because of the more uniformly burned and smaller-particle-size product. Rotary kilns are also necessary for burning "lime sludge" from paper and sugar mills. Complete rotary-kiln plants usually require an investment of $1,400 per daily ton of lime capacity. The trend to larger plants is well illustrated by the fact that the number of operating plants decreased from approximately 900 in 1915 to about 350 in 1940 and 182 in 1946. About 60 per cent of the 1946 plants (182) had capacities less than 25,000 tons yearly but produced less than 15 per cent of the total lime production.

Kiln operation is not simple, since overheating the charge leads to "dead-burned" or semivitreous materials, and underheating may leave unconverted carbonate in the product ("underburned" lime). The preferred raw material for chemical lime is high-calcium limestone, except for the sulfite pulp industry, where some magnesium oxide is preferable. Silicious and aluminous impurities tend to increase "dead burning."



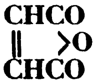
Location of Lime Plants

A considerable amount of chemical lime appears on the market as "hydrated" lime. In general, the hydration process is most effectively carried out on a large scale (4 to 5 tons per hour) because of the relative difficulty of removing impurities in small-scale operations. Fresh lime also hydrates more readily than lime that has stood in the air. A variety of hydrators, differing only in mechanical details, are on the market. Intermittent hydrators generally produce 1.5 tons of hydrated lime per batch. Of the lime sold in the open market, about 80 per cent is quicklime, and the remainder hydrated lime.

Marble and oyster shells are also used as raw materials, with the latter producing very high-grade chemical lime. Gas and oil are preferred fuels for high-quality limes, chiefly because of cleanliness.

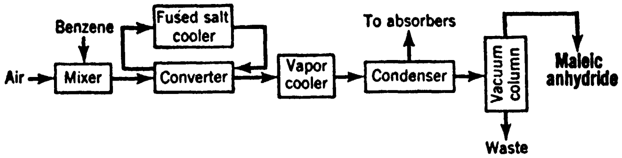
In the chemical industry, lime is principally used as an alkali and is competitive with caustic soda, soda ash, and ammonia. The chief drawbacks of lime as a neutralizing agent for acidic solutions are its low solubility in water and the formation of insoluble salts (except where anion removal is advantageous). Its chief advantage is its low price.

MALEIC ANHYDRIDE

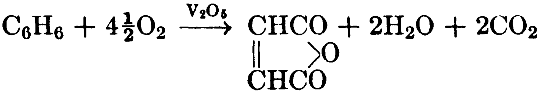


$$\begin{array}{l}\text{CHCO}\\ \| \quad \rangle\text{O}\\ \text{CHCO}\end{array}$$

From Benzene by Catalytic Vapor-Phase Oxidation



Reaction



$$C_6H_6 + 4\tfrac{1}{2}O_2 \xrightarrow{V_2O_5} \begin{array}{l}\text{CHCO}\\ \| \quad \rangle\text{O}\\ \text{CHCO}\end{array} + 2H_2O + 2CO_2$$

50–60% yield

Material Requirements

Basis—1 ton maleic anhydride

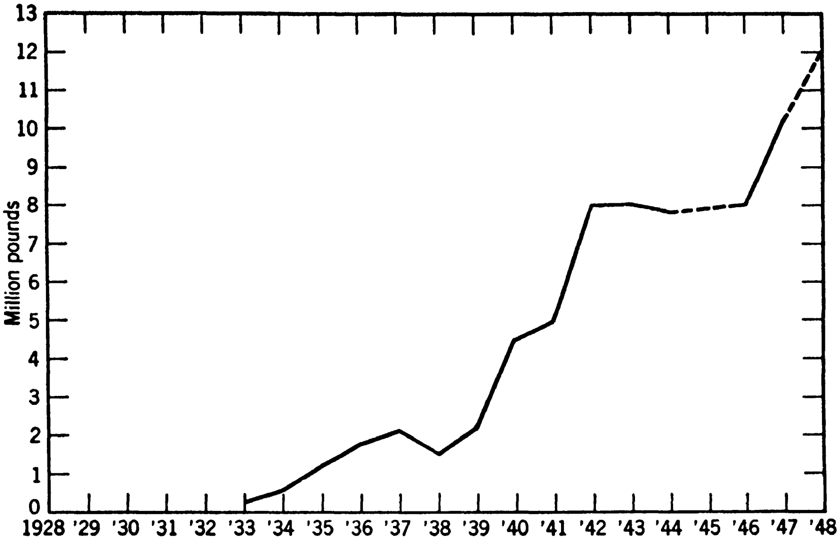
Benzene	2,680 lb
Air	500,000–700,000 cu ft (STP)

Process

Benzene is catalytically oxidized to yield maleic anhydride in a manner similar to the production of phthalic anhydride by naphthalene oxidation.

Compressed air (2 to 3 atm) is fed to a mixer where a measured stream of benzene is added under such conditions that the benzene is vaporized and the correct benzene–air ratio is obtained. The mixer may consist of a coil immersed in hot water or steam through which the reactants are fed. Theoretically, about 106 cu ft of air is required per lb of benzene oxidized. Generally much higher ratios (2 to 5 times) are used.

The vapor mixture is blown through a multitubular converter, containing vanadium pentoxide catalyst supported on an inert carrier such as aluminum turnings or diatomaceous earth. The reaction is highly exothermic, and, once initiated, it is self-supporting. A temperature of 400 to 450°C is maintained by efficient heat removal. The heat liberated ranges from 10,500 to 13,500 Btu per lb of benzene reacted. Special cooling means are used, such as circulating mercury or fused salts across the tube banks. The contact time is approximately 0.1 sec at about 1 atm pressure and a temperature between 400 and 450°C.



Production—Maleic Acid and Anhydride

The reaction gases, consisting mostly of a maleic anhydride–maleic-acid mixture, carbon dioxide, water, and some unreacted benzene, pass through a vapor cooler.

The recovery apparatus differs from plant to plant and depends on the nature of the product desired. If maleic acid is to be the sole product, the cooled gases are absorbed in water to yield about a 40 per cent maleic-acid solution. After a purifying treatment using decolorizing carbon, the solution may be partially evaporated and crystallized to yield crystalline maleic acid.

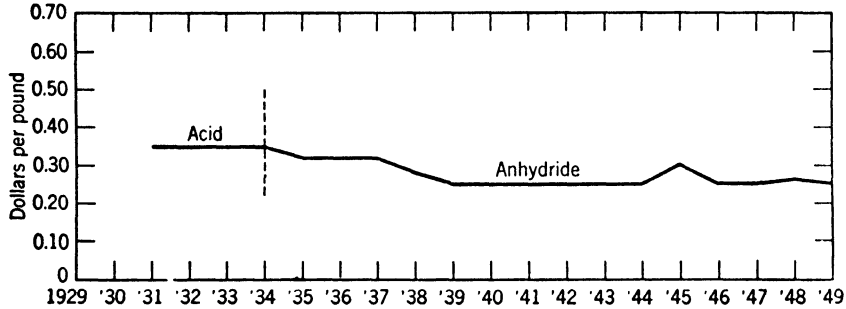
There are several methods for obtaining maleic anhydride as the main product, and many modifications of these methods have been reported. One such process is to pass the cooled vapors through a partial condenser maintained at a temperature slightly above the melting point of maleic anhydride (60°C). Most of the maleic acid and anhydride are condensed, and the remaining vapors pass to an absorber. Here the gases are absorbed in either aqueous or nonaqueous solvents. Hydrocarbons such as benzene or high-boiling esters may be used to absorb the anhydride, which may then be recovered by dehydration and distillation.

The bulk of maleic anhydride is recovered in the condensers and contains varying amounts of maleic acid. This is converted to the anhydride by removing the water by vacuum or azeotropic distillation (using hydrocarbons). The removal of the water by direct heat is not practical, since maleic acid gradually changes to fumaric acid when heated above its melting point. The crude maleic anhydride may be packaged or first purified by vacuum distillation or sublimation. The yield of maleic anhydride based on benzene is 50 to 60 per cent.

Maleic anhydride is also obtained as a by-product in the oxidation of naphthalene. See *Phthalic Anhydride* for details.

Use Pattern

	1947 (est.), per cent
Synthetic resins	85
Chemicals and miscellaneous	15
	100



Price—Maleic Anhydride

Miscellaneous

Properties. White needles or flakes.

Mol. wt.	98.06	M.P.	53°C
Sp. gr.	0.934 20°C/4	B.P.	199.7°C

Soluble in acetone, ether, chloroform, and petroleum hydrocarbons. Very slightly soluble in carbon tetrachloride. Soluble in water (16.3 g per 100 g at 30°C).

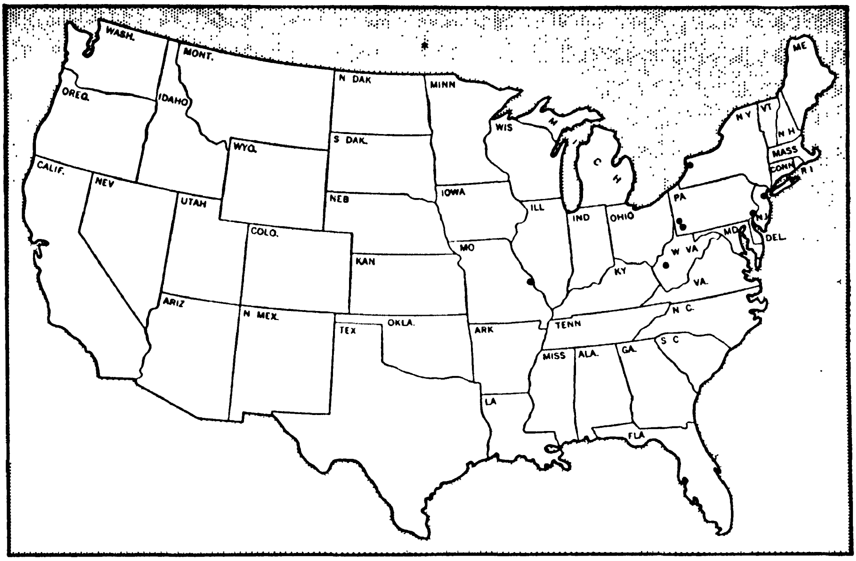
Flash point (open cup) 240°F

Grades. Commercial (99 per cent), as flakes, pellets, briquets, or solidified in container.

Containers and Regulations. Barrels, tins, and bottles. No ICC shipping label required.

Economic Aspects

For years benzene has been the preferred raw material for maleic anhydride manufacture, although before World War II one manufacturer used a mixture of butylenes and butadiene. Actually, almost any four- or five-carbon organic chemical, except the paraffin hydrocarbons, yields maleic anhydride by vapor-phase oxidation over vanadium catalysts.



Location of Maleic Anhydride Plants

Furfural, crotonaldehyde, and olefins are particularly satisfactory, but price still favors benzene.

For resin manufacture, maleic anhydride may be considered a competitor of phthalic anhydride, and numerous resins developed during World War II (pentaerythritol–maleic anhydride resins, for instance) may increase in use. Price, again, still favors phthalic anhydride.

Considerable maleic anhydride was used during World War II in the manufacture of substitute drying oils. As long as the higher-grade oils are in short supply, such practice will probably continue. The amount of maleic anhydride that will be so employed when these oils are in better supply is debatable. On the other hand, the possibilities offered by the Diels-Alder synthesis foreshadow considerable further demand for maleic anhydride.

The various other acids derived from maleic anhydride, such as succinic, malic, and fumaric acids, also may find increased demand in the future. For fumaric-acid production, a fermentation process is competitive. It is also possible to recover fumaric acid directly from benzene oxidation gases, if the converter exit gases are scrubbed with hydrochloric-acid solution.

Maleic anhydride plants are similar to but smaller than those used for phthalic anhydride production and require about a 20 per cent greater investment than phthalic anhydride plants because of the difference in yield (see *Phthalic Anhydride*).

Maleic anhydride is also recovered as a by-product of phthalic anhydride production, and it is possible that a change in catalyst could produce a larger proportion.

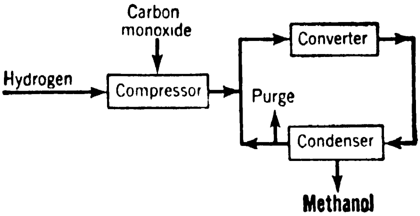
The chief variation in the maleic anhydride process from one manufacturer to another is in converter design, which depends largely on the coolant used. Mercury, diphenyl, and fused salts are the most popular heat-removal agents.

METHYL ALCOHOL

(METHANOL)

CH_3OH

From Carbon Monoxide and Hydrogen



Reaction

$$CO + 2H_2 \rightarrow CH_3OH$$

60% yield (without recycle)

Material Requirements

Basis—1 ton methanol

Carbon monoxide	37,400 cu ft (STP)
Hydrogen	75,390 cu ft (STP)

Process

Methanol is synthesized by the reaction of hydrogen and carbon monoxide under high pressures. The reactants, hydrogen and carbon monoxide, are obtained in a variety of ways from different raw materials. The more important of these sources are:

1. Coal and water to produce first coke and then blue-water gas, which contains about equal proportions of hydrogen and carbon monoxide. The water gas is purified and fortified with additional hydrogen obtained from coke-oven gas. (See *Ammonia* for details.)

2. Re-formed natural gas.

3. Fermentation by-product gases. Hydrogen and carbon dioxide are obtained in about equal proportions. The latter may be converted to carbon monoxide by passing it over a hot bed of coke. (For details, see *Acetone* and *Butyl Alcohol.*)

4. By-product gases (carbon monoxide) from calcium carbide furnaces. (See *Acetylene.*)

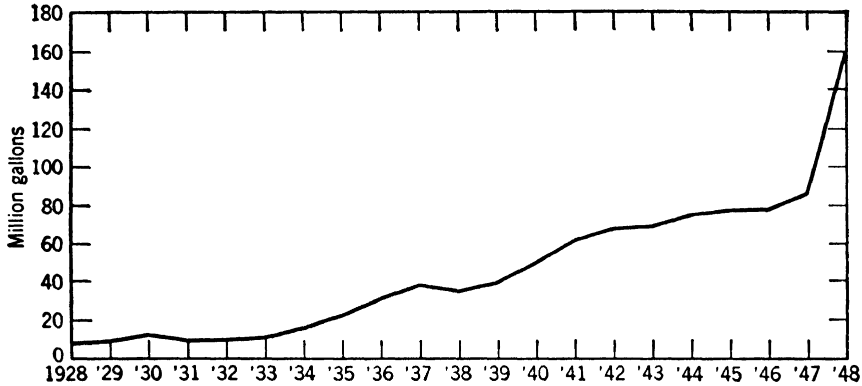
5. Hydrogen is also obtained by the electrolysis of water and brine. (See *Hydrogen.*)

6. A few plants use carbon dioxide instead of carbon monoxide. The methanol reaction in this case is:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$$

(For raw-material sources, see *Carbon Dioxide.*)

The following description is limited to the carbon monoxide process: The gas mixture obtained from one or more of the afore-mentioned sources is adjusted so that approximately the theoretical ratio is obtained (two volumes of hydrogen to one volume of carbon monoxide). The mixed gases are compressed in multistage compressors to pressures of 3,000 to 5,000 psi and heated in heat exchangers by the reaction gases. The heated gases pass through a copper-lined steel converter containing a mixed catalyst of the oxides of zinc, chromium, manganese, or aluminum: for example, zinc oxide with 10 per cent chromium oxide. The temperature of the reaction is maintained at approximately 300°C by proper heat removal from the exothermic reaction (24,620 cal per g mole of methanol). The converter must be heated to initiate the reaction, but, once started, it is self-supporting. The temperature is kept constant by proper space velocity and heat interchange.



Production—Methanol (Synthetic and natural)

The methanol-containing gases leaving the reactor are cooled by the reactants in heat exchangers and condensed under full operating pressures. The pressure is released, and the cool (0 to 20°C) liquid methanol is run off. It may be further purified by distillation. The residual gases are returned to the system for reprocessing. Accumulation of inert gases is guarded against by purging a part of the recycle gases. Methanol of 99 per cent purity is obtained, using this process, and the equilibrium yield is better than 60 per cent.

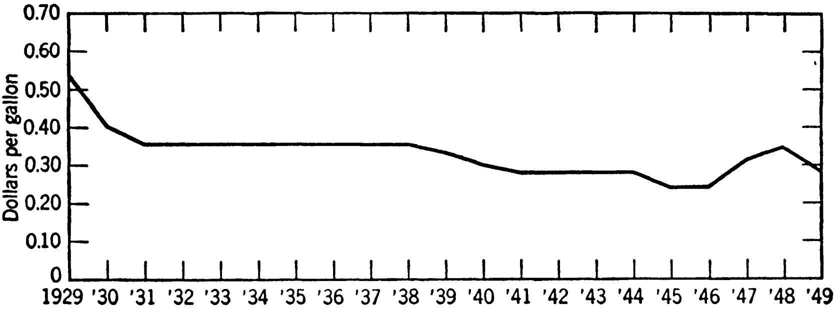
In the carbon dioxide–hydrogen process, the crude methanol product containing about 25 per cent water is sent to a continuous refining column where an overhead cut, consisting of ethers and some methanol, is removed. The bottoms are sent to a second column where methanol is removed overhead and water is removed as bottoms. A side cut is removed from near the bottom of the column. This cut consists of 30 per cent methanol, 50 per cent higher alcohols including ethyl alcohol, and 20 per cent water.

Synthetic methanol is also produced by the incomplete combustion of natural gas. For details, see *Acetaldehyde.*

Natural methanol (wood alcohol) is obtained from hardwood distillation. For details, see *Acetic Acid.*

Use Pattern

	1947 (est.), per cent
Formaldehyde	45
Dimethylamine and dimethylaniline	5
Antifreeze	40
Denaturant	5
Miscellaneous and solvent	5
	100



Price—Methanol

Miscellaneous

Properties. Clear, colorless, flammable, volatile, very mobile liquid. Poisonous when taken internally.

Mol. wt.	32.04	M.P.	−97.8°C
Sp. gr.	0.792 20°C/4	B.P.	64.7°C

Weight per gallon 6.59 lb (20°C)

Soluble in water, alcohol, and ether in all proportions.

Flash point (closed cup)	52°F
Ignition temperature	800°F
Vapor density (air = 1)	1.11
Explosive limits (% by volume in air)	Lower 6.0 Upper 36.5

Grades. Pure (acetone-free, 99.8 per cent), crude (wood spirit), C.P., USP, 95 per cent, and 97 per cent.

Containers and Regulations. Tank cars, tank trucks, drums, barrels, cans, and bottles. Red ICC shipping label required.

Economic Aspects

Before 1926 all American commercial methyl alcohol or wood alcohol was recovered as a by-product of the wood-distillation industry. In 1926 thousands of gallons of German synthetic methanol appeared on the New York market at half the current price of wood alcohol, thus accelerating the demise of the wood-distillation industry. Since that time the synthetic-methanol industry has grown rapidly, until in 1940 only 9 per cent of United States methanol production was by the wood-distillation industry. In 1947 this figure had decreased to less than 3 per cent.

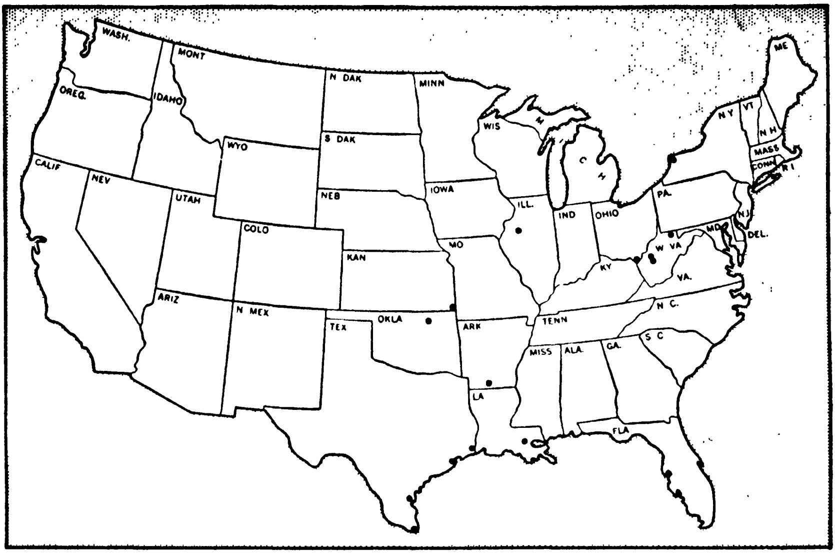
Variations in synthetic-methanol plants from one manufacturer to another are similar to those in synthetic-ammonia plants. Source of hydrogen and operating conditions are the chief variables. The majority of plants use water gas or re-formed natural gas as the raw material and operate between 3,000 and 4,000 psi. Higher alcohols are produced as by-products in all processes but are favored by iron-containing catalysts and high temperatures. Many ammonia plants are so designed that methanol may be made alternately with few equipment changes.

In general, wood alcohol is costly to refine, and, accordingly, it is used chiefly for antifreeze and as a denaturant for ethyl alcohol. The yield of crude methyl alcohol is generally figured as 10 gal per cord of hardwood (airdried basis).

The threat of methanol manufacture from methane is not sufficient to warrant predictions of replacement of the existing process, but there is little doubt that inroads may be made by the oxidation of propane and butane (see *Acetaldehyde*) and to less extent by the Fischer–Tropsch process. The latter process, for which at least one plant is under construction, produces large quantities of oxygenated organic chemicals as a by-product of gasoline and oil. In general, however, these chemicals contain two or more carbon atoms per molecule.

Considerable expansion for most of the uses of methanol may be expected in the near future. Solvent uses, however, will be limited because of the poisonous nature of methanol vapors. The chief new use for methanol, and perhaps a large one, may be in the manufacture of jet and rocket fuels.

Synthetic-methanol manufacture is a large-scale industry, and most production is from plants varying in size from 10,000,000 to 30,000,000 gal annual capacity. Plant investment required is in the neighborhood of 50 to 60 cents per gallon annual capacity. The largest-known plant has an annual capacity of 70,000,000 to 80,000,000 gal but is operating at a much reduced capacity.



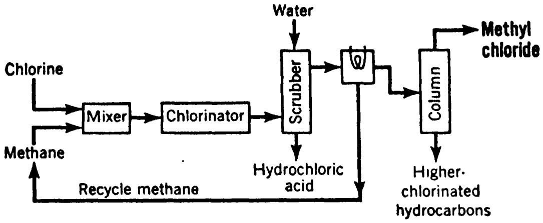
Location of Synthetic-Methanol Plants

METHYL CHLORIDE

(CHLOROMETHANE)

CH_3Cl

From Methane by Chlorination



Reaction

$$CH_4 + Cl_2 \xrightarrow{\text{Catalyst}} CH_3Cl + HCl$$

80% yield

Material Requirements

Basis—1 ton methyl chloride

Chlorine	3,700 lb
Methane (STP)	18,500 ft
Catalyst makeup	Small

Process

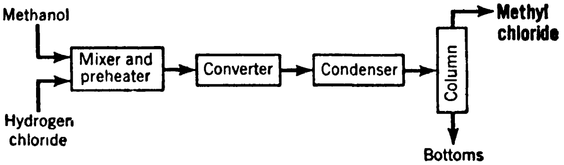
The reaction between chlorine and methane in the presence of a catalyst may be so controlled as to yield predominantly methyl chloride, with the formation of smaller amounts of methylene chloride, chloroform, and carbon tetrachloride.

Methane, obtained by purifying natural gas, is mixed with dry chlorine gas in a 10-to-1 volume ratio. From the mixer, the gases pass through a chlorination furnace operated at about 450°C. Various catalysts may be used for the reaction, such as partially reduced cupric chloride or pumice. The contact time varies but is usually maintained in the range of 1 to 20 sec.

The reaction gases pass through a water scrubber to remove the hydrogen chloride formed and are then led through a series of water-cooled and refrigerated condensers under pressure. The mixture of chlorinated hydrocarbons condenses, and unreacted methane is recycled to the mixing chamber. Practically all the chlorine reacts with the methane, so that little or no chlorine remains in the reaction gases.

Crude methyl chloride is distilled under pressure to yield pure methyl chloride of refrigerant grade. Approximately 85 to 90 per cent of the condensate distils between −23 and −25°C (atmospheric pressure) to give a yield of methyl chloride of about 80 per cent based on the chlorine charged.

From Methanol and Hydrogen Chloride



Reaction

$$CH_3OH + HCl \xrightarrow{\text{Catalyst}} CH_3Cl + H_2O$$

90–95% yield

Material Requirements

Basis—1 ton methyl chloride

Methanol	1,400 lb
Hydrogen chloride	1,600 lb
Alumina gel	Small

Process

Methyl chloride is produced by the action of hydrogen chloride on methanol, with the aid of a catalyst, in either the vapor or the liquid phase.

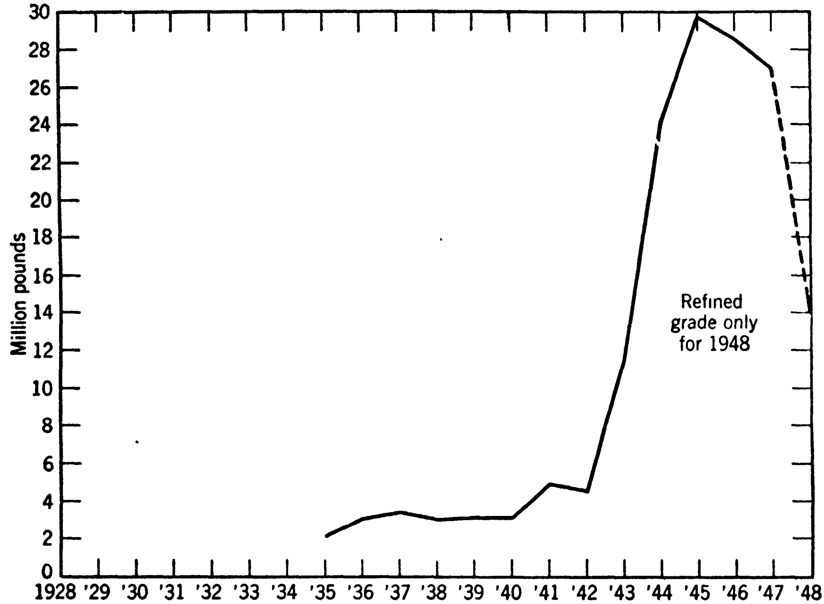
Vapors of methanol and hydrogen chloride are continuously mixed in approximately equimolecular ratios and passed through a preheater maintained at about 180°C. The gas mixture is then passed at substantially atmospheric pressure through a converter at a temperature of 340 to 350°C. The converter is packed with previously ignited alumina gel of 8- to 12-mesh size or a similar-acting catalyst, such as zinc chloride on pumice, cuprous chloride, or activated carbon. The converter is externally heated by electric coils or some other suitable means. Space velocities of about 275 cu ft per hr per cu ft of gross catalyst volume are generally used (based on gas volumes at STP).

The hot reaction gases leaving the converter are passed through condensers, where they are collected and purified in a manner similar to that previously described.

The yield of methyl chloride based on alcohol used is about 95 per cent of theoretical.

In the liquid phase at 100 to 150°C, methyl chloride may be produced by refluxing and distilling an aqueous mixture, which contains methanol, hydrogen chloride, and zinc chloride. An 80 per cent yield by volume results.

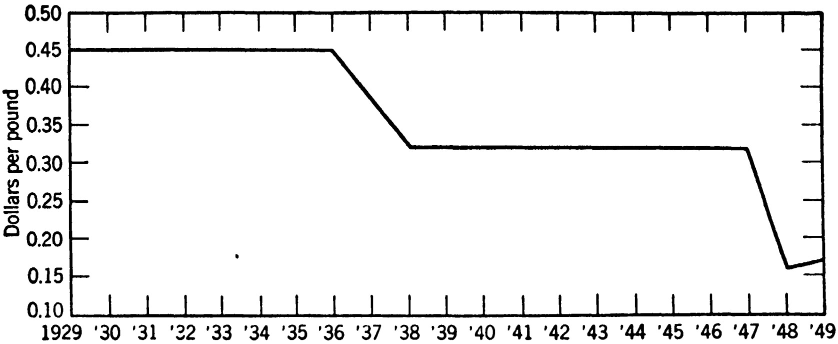
An alternate procedure uses 1 mole of aluminum chloride and 1 mole of methanol. After heating at 80 to 90°C for a few hours, hydrogen chloride is freely given off. If the temperature is slowly raised to 140°C, the reaction becomes very rapid, and methyl chloride is distilled and collected. An 80 to 90 per cent yield is realized based on methanol.



Production—Methyl Chloride (Crude and refined)

Use Pattern

	Per cent
Organic intermediate and solvent	80
Refrigeration	20
	100



Price—Methyl Chloride

Miscellaneous

Properties. Colorless, noncorrosive, liquefiable gas, which is colorless in the liquid state. Has a faintly sweet, ethereal, nonirritating odor.

Mol. wt.	50.49	M.P.	−97.7°C
Sp. gr.	0.920 20°C/4	B.P.	−24.1°C

Weight per gallon 7.68 lb (20°C)

Soluble in water (280 cc per cc at 17°C), alcohol 3,500 cc per cc at 20°C), acetone (4,000 cc per cc), chloroform, and ether.

Flash point (closed cup)	Gas
Ignition temperature	1,170°F
Vapor density (air = 1)	1.78
Explosive limits (% by volume in air)	Lower 8.2 Upper 19.7

Grades. Technical (99.9 per cent).

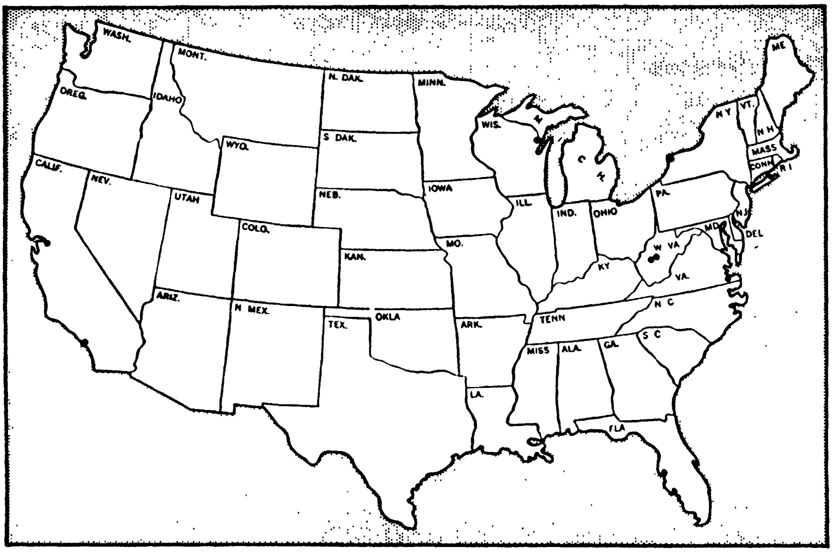
Containers and Regulations. Tank cars, drums, and cylinders. Toxic gas at 15 to 30 per cent concentration by volume. Red gas ICC shipping label required.

Economic Aspects

The methanol process is by far the more important of the two processes used for methyl chloride production. It is only under those conditions where both cheap natural gas and cheap chlorine are available that direct chlorination of methane is competitive. The three other chlorinated products obtained, methylene dichloride, chloroform, and carbon tetrachloride, must also be recovered. In Europe, methyl chloride has been produced by the treatment of betaine-rich residual liquors from beet-sugar molasses, but the process does not appear to be economical in the United States.

In one of its major uses, as a refrigerant, methyl chloride must compete with a variety of other materials, the chief one of which is dichlorodifluoromethane ("Freon-12"). As an intermediate, however, some increase in use may be expected with the continued growth of the synthetic-organic-chemical industry.

Based on production figures, it appears probable that plants vary in size from 1,000,000 to 10,000,000 lb annual capacity, although smaller plants may still be economical. Plants hydrochlorinating methanol and in the size range from 5,000,000 to 10,000,000 lb annual production cost approximately $20,000 per 1,000,000 lb per yr capacity.



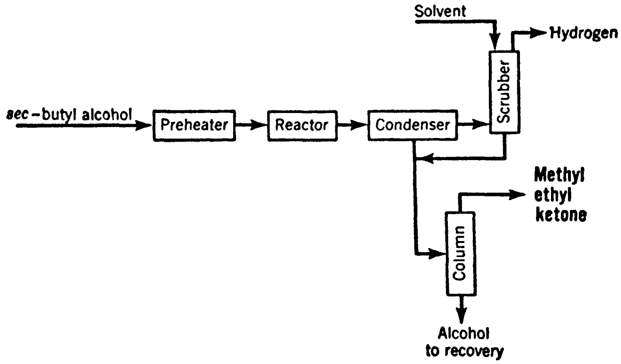
Location of Methyl Chloride Plants

METHYL ETHYL KETONE

(BUTANONE-2)

$CH_3COCH_2CH_3$

From Secondary Butyl Alcohol by Dehydrogenation



Reaction

$$CH_3CH(OH)CH_2CH_3 \rightarrow CH_3COCH_2CH_3 + H_2$$

85–90% yield

Material Requirements

Basis—1 ton methyl ethyl ketone

sec-Butyl alcohol	2,350 lb

Process

Methyl ethyl ketone (MEK) is obtained by the dehydrogenation of secondary butyl alcohol in a process analogous to the production of acetone from isopropyl alcohol.

Preheated vapors of secondary butyl alcohol are passed through a reactor, containing a catalytic bed of zinc oxide or brass (zinc–copper alloy) maintained at 400 to 550°C. The reaction takes place at atmospheric pressure.

The reaction gases are condensed by passage through a brine-cooled condenser. The uncondensed gas may be scrubbed with water or a nonaqueous solvent to remove any entrained ketone or alcohol from the hydrogen-containing gas.

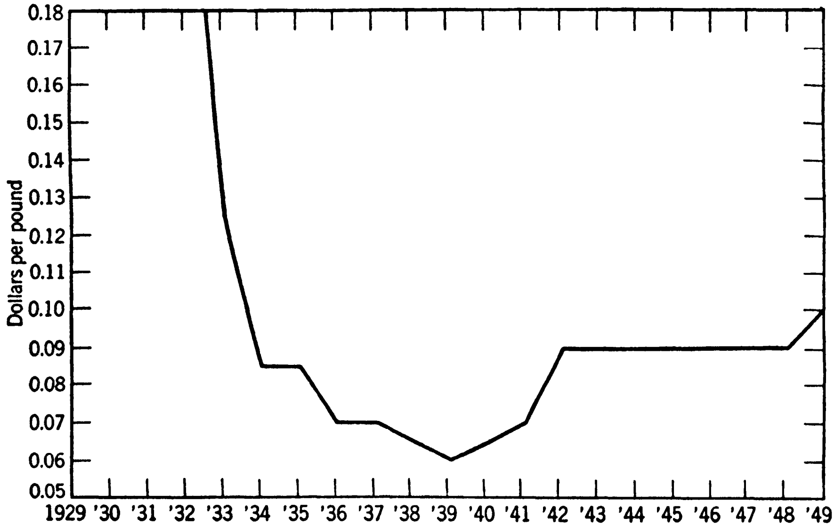
The condensed product is run into a distilling column and fractionated. The main fraction (methyl ethyl ketone), boiling between 78 and 81°C, is obtained in an 85 to 90 per cent yield based on the weight of secondary butyl alcohol charged.

Production

No figures available.

Use Pattern

	Per cent
Coatings	85
Miscellaneous	15
	100



Price—Methyl Ethyl Ketone

Miscellaneous

Properties. Colorless, flammable liquid possessing an acetone-like odor.

Mol. wt.	72.10	M.P.	−85.9°C
Sp. gr.	0.805 20°C/4	B.P.	79.6°C

Weight per gallon 6.7 lb (20°C)

Soluble in water (37 g per 100 g at room temperature), alcohol, ether, acetone, and benzene. Miscible with oils.

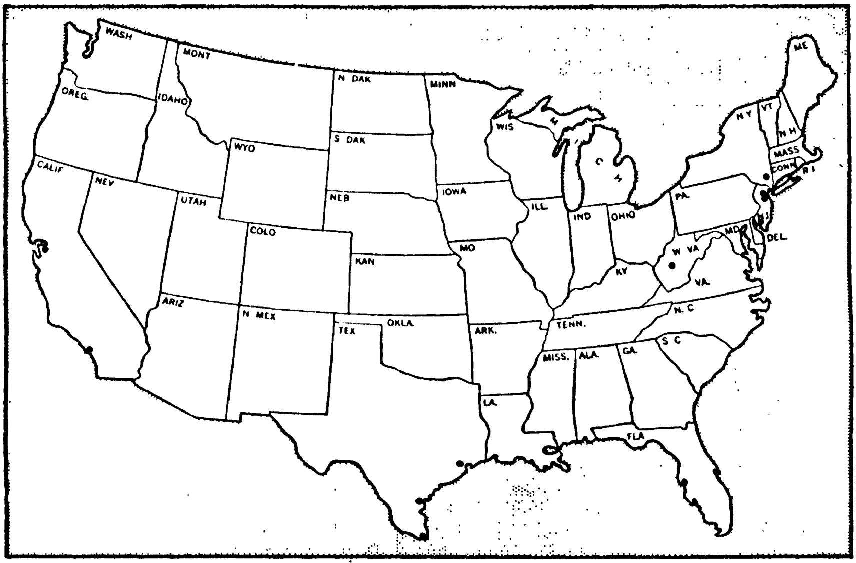
Flash point (closed cup)	30°F
Vapor density (air = 1)	2.41
Explosive limits (% by volume in air)	Lower 1.81
	Upper 11.5

Grades. Technical, and C.P.

Containers and Regulations. Tank cars, drums, barrels, tins, and bottles. Red ICC shipping label required.

Economic Aspects

In general, methyl ethyl ketone (MEK) may be used for the same purposes as acetone, where a ketone with lower vapor pressure is required. Demand for use in cellulose finishes and in vinyl resin coatings has been especially active. Expansion during the war years was primarily caused by demand for high-grade military coatings of various types.



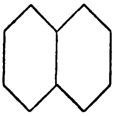
Location of Methyl Ethyl Ketone Plants

Practically all methyl ethyl ketone is made today by the dehydrogenation of *sec*-butyl alcohol. The older method of distilling methyl acetoacetate in the presence of sulfuric acid is no longer used. A small amount of MEK is recovered from the liquid product of hydrocarbon oxidation (see *Acetaldehyde*). MEK should not be confused with "methyl acetone," a solvent mixture (25 to 30 per cent methanol, 40 to 50 per cent acetates, 25 to 40 per cent acetone), obtained as a by-product in the wood-distillation industry.

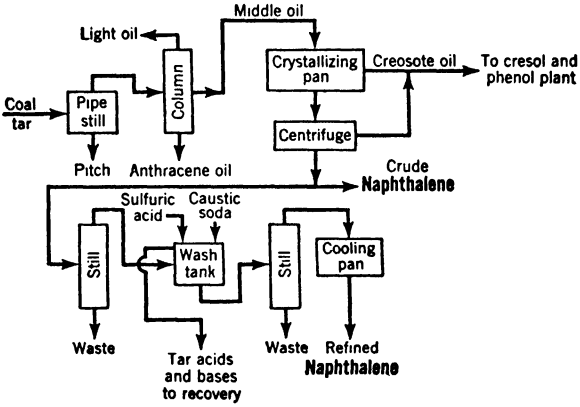
Future demand for MEK will depend on price decreases and new uses developed as the material is studied more widely. As production increases, it may present a serious threat to ethyl acetate as a lacquer solvent.

Plant investment costs are probably in the same range as those for synthetic acetone derived from isopropyl alcohol (see *Acetone*).

NAPHTHALENE



From Coal Tar



Recovery

10% of coal tar weight

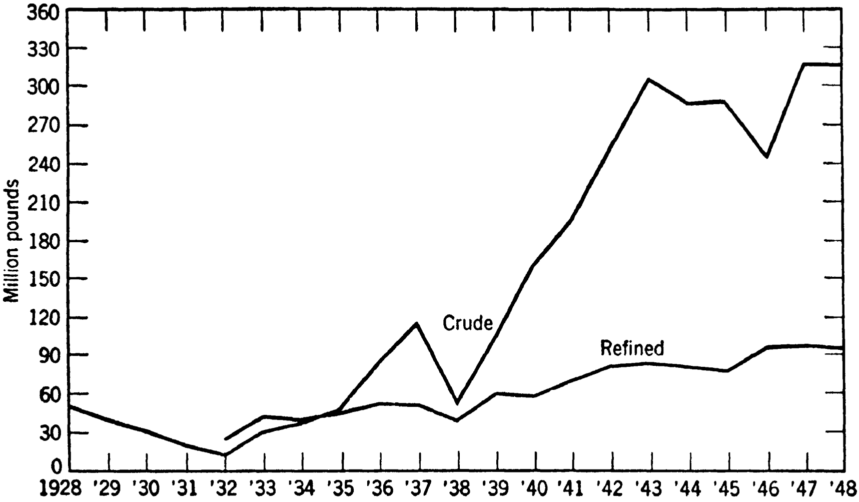
Process

Naphthalene is obtained by the distillation of coal tar (*ca.* 10 gal per ton of coal) recovered in the by-product coking of coal. See *Coke* for details on coal-tar recovery. Some of the recovered tar is sent to refineries where it is distilled, yielding several fractions that are purified further. In an ordinary batch distillation, the following fractions (and average yields based on the original tar) are commonly obtained:

5 per cent light oil	Up to 200°C
17 per cent middle oil	200–250°C
7 per cent heavy oil	250–300°C
9 per cent anthracene oil	300–350°C
62 per cent pitch	Residue

The middle-oil or creosote-oil fraction (200 to 250°C) serves as the most abundant source of naphthalene, although smaller amounts are present in both the light and heavy oils. The amount of naphthalene present in coal tar is approximately 10 per cent, which is by far the largest percentage of any single chemical compound.

The crude coal tar is generally distilled in continuous tube or pipe stills to give the desired type of residue (pitch). These stills consist essentially of a battery of tubes, arranged within a furnace, through which the tar is pumped (under pressure) in a continuous stream at a relatively high velocity. The tar is discharged into a flash box from which the vapors pass to condensers or fractionating columns, while the pitch runs continuously to receiving tanks. Since the tar remains in the tubes for only a few minutes, there is a minimum of overheating, producing small percentages of free carbon. If the total distillate is condensed, it must be further processed by distilling in either batch or continuous stills, depending on the volume and grades of tar processed. Generally three or four fractions are taken: namely, light oils (see *Benzene*, *Toluene*, and *Xylene*), middle oils, and heavy oils (naphthalene, also see *Cresol* and *Phenol*), and anthracene oils. The last fraction is often combined with the heavy-oil cut.



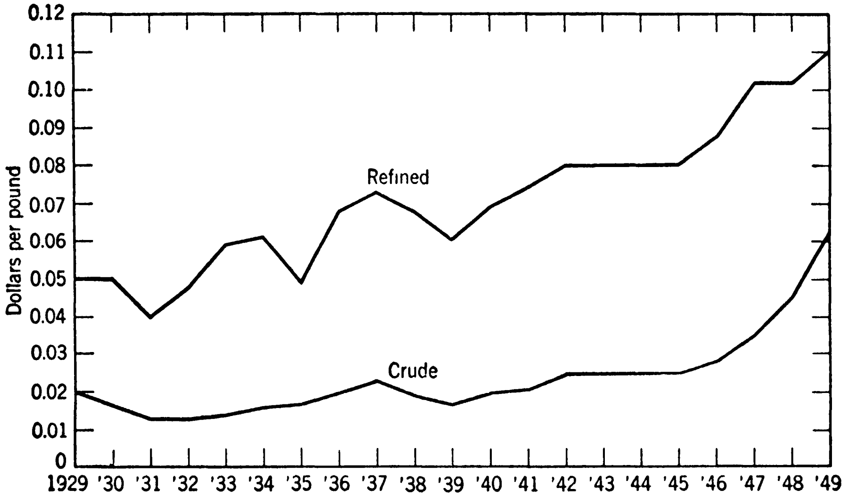
Production—Naphthalene

The middle-oil fraction, containing most of the naphthalene and tar acids (phenols and cresols), is pumped hot into shallow, rectangular pans, where it is allowed to cool so that the naphthalene may crystallize. After draining, the crystalline cake is broken up and charged into batch centrifuges. The mother liquor is combined with the crystallizing pan drainings and sent to cresol- and phenol-recovery units. The naphthalene cake may be washed with hot water to increase its purity and is then discharged as crude naphthalene. This material is suitable for phthalic anhydride manufacture and is graded and sold according to its melting point (generally 74, 76, and 78°C).

For refined naphthalene (m.p. above 79°C), the crude material is distilled. The distillate is passed to a wash tank where it is agitated first with hot caustic-soda solution to remove phenolic bodies (tar acids) and then with concentrated sulfuric acid to remove basic substances (pyridines). The washed naphthalene is sublimed or redistilled to yield refined naphthalene. The final purification step varies according to the product specifications. If the washed naphthalene is distilled, the distillate is either cast into forms or allowed to cool and is subsequently crushed.

Use Pattern

	1947 (est.), per cent
Phthalic anhydride	63
β-naphthol	20
Moth repellent	7
Miscellaneous	10
	100



Price—Naphthalene

Miscellaneous

Properties. White, crystalline, volatile flakes or powder possessing a strong coal-tar odor.

Mol. wt.	128.16	M.P.	80.2°C
Sp. gr.	1.145 20°C/4	B.P.	217.9°C

Soluble in benzene, absolute alcohol, ether, chloroform, and carbon disulfide. Slightly soluble in alcohol (9.5 g per 100 g at 19.5°C). Very slightly soluble in water (0.003 per cent at 25°C).

Flash point (closed cup)	176°F
Ignition temperature	1,038°F
Vapor density (air = 1)	4.42
Explosive limits (% by volume in air)	Lower 0.9

Grades. Crude, refined, USP, and C.P. in the form of flakes, balls, blocks, cubes, grains (rice), powder (crushed), and tablets.

Containers and Regulations. Crude: tank cars and bags. Refined, USP and C.P.: barrels, bags, cases, cans, and bottles. No ICC shipping label required.

Economic Aspects

Naphthalene may well be considered the basic coal-tar derivative for the dye industry because, unlike phenol, its only source is the destructive distillation of coal. It is, however, only one of a number of organic chemicals derived from this source (see *Phenol, Cresol, Benzene, Toluene, Xylene*). Standard naphthalene yields from vertical gas retorts are 2 lb per ton of coal; coke ovens, 6 lb per ton of coal, high-temperature horizontal gas retorts, 11 lb per ton of coal. On the basis of coal tar, the usual yield of crude naphthalene is 40 lb per 100 gal. Refined naphthalene yield is about 80 per cent of the crude. In 1947 tar distillers produced 75 per cent of total naphthalene production; coke-oven operators the remainder. More naphthalene could probably be recovered than is at present and would be if the price were sufficiently attractive. In this connection, it is not unreasonable to believe that increasing demands for naphthalene derivatives will lead to (1) increased recovery and possibly higher prices for coal-tar naphthalene, (2) marked attempts to recover naphthalene from petroleum, (3) further efforts to synthesize naphthalene derivatives by other methods, and (4) replacement of naphthalene derivatives by other chemicals.

Before any of these things happen, however, naphthalene for moth balls may be replaced by *p*-dichlorobenzene and other pesticides, leaving naphthalene for chemical uses.

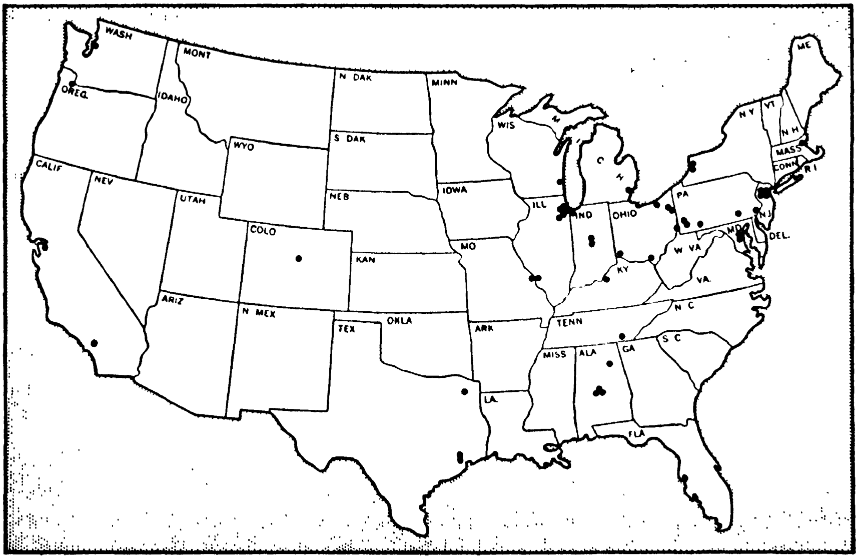
A further long-time threat to cheap naphthalene is the possibility of a decrease in steel production because of competition with aluminum, magnesium, and plastics.

By-product coking yields about 8 to 12 gal of coal tar per ton of coal. A portion of this tar is sold to coal-tar distillers who may be either independent or subsidiaries of the by-product coke industry. It is estimated that about 70 per cent of the tar is collected in the hydraulic and section mains of the by-product coke plant, 21 per cent in the primary coolers, and 9 per cent by electric precipitation.

Distillation of coal tar yields four fractions: light oils (benzene, toluene, and homologs); middle oils, or creosote oils, containing naphthalene and tar acids (phenol, cresols, etc.); anthracene oil; and pitch. Distillation is carried out in all sorts of stills, ranging from the older fire-heated batch stills (3,000 to 7,000 gal capacity) to modern continuous pipe stills.

Whether coal tar is sold to distillers or used as fuel depends on economic conditions and the relative value of the two operations. Before World War II, about 60 per cent of the tar produced was refined. In 1946 this figure had risen to 87 per cent.

Low-temperature distillation of coal using Curran-Knowles ovens is said to yield tar containing 4.25 per cent acids, compared with 1 per cent in tar from high-temperature coking. Other economic factors, however, have hindered establishment of low-temperature coking on anything but a minor scale.

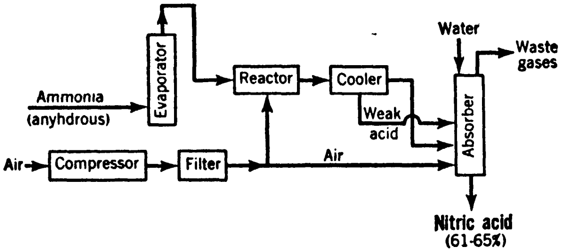


Location of Naphthalene Plants

NITRIC ACID

HNO_3

From Ammonia



Reaction

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

$$2NO + O_2 \rightarrow 2NO_2$$

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

93–95% yield

Material Requirements

Basis—1 ton nitric acid (100%)

Ammonia (anhydrous)	575 lb
Platinum	0.01–0.02 oz
Air	115,000 cu ft

Process

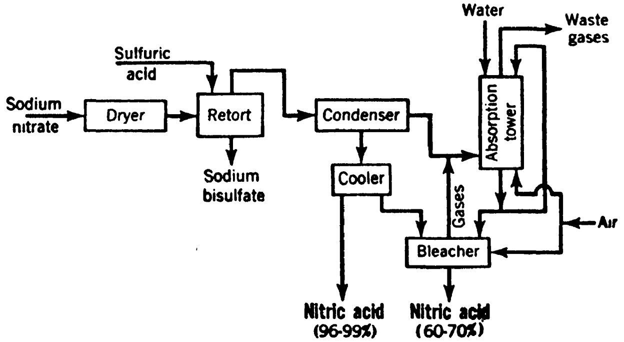
Air is compressed to approximately 100 psi, filtered, and preheated to about 300°C by passing through a heat exchanger. It is mixed with anhydrous ammonia, previously vaporized in a continuous-steam evaporator. The resulting mixture, containing about 10 per cent ammonia by volume, is passed through the reactor, which contains a platinum–rhodium (2 to 10 per cent rhodium) wire-gauze catalyst. The platinum–rhodium alloy is used in the form of a very fine gauze, 80-mesh by 0.003-in.-diameter wire, packed in layers (10 to 30 sheets), so that the gas travels downward through the gauze sheets. The catalyst temperature is about 750°C, the pressure 100 psi, and the contact time about 3×10^{-4} sec.

The hot nitric oxide and excess air mixture (about 15 per cent nitric oxide) from the reactor is partially cooled in a heat exchanger and further cooled in a water cooler. The cooled gas is introduced into a stainless-steel absorption tower with more air being added for the further oxidation of nitric oxide to nitrogen dioxide. Since the equilibrium of this reaction is more favorable at lower temperatures, most of the reaction occurs in the absorption tower, which is continuously cooled externally with water. Small quantities of water are added to hydrate the nitrogen dioxide and partially to scrub the gases. The gas from the top of the tower generally is heated in a heat exchanger and then expanded through a power-recovery compressor for part of the air supply before being released to the atmosphere.

The bottom of the tower yields nitric acid of 61 to 65 per cent strength, which may be concentrated if so desired. This may be done in silicon–iron or stoneware towers by feeding 66°Bé sulfuric acid to the top and 61 to 65 per cent nitric acid below the top. The vapor leaving the tower is 90 per cent nitric acid or better, whereas the bottoms consist of dilute (70 to 75 per cent) sulfuric acid.

Most modern plants operate under positive pressure (100 psi) rather than at atmospheric pressure because of the increase in acid strength obtained (about 15 per cent), the fiftyfold increase in the rate of reaction, and the great decrease in tower volume required for oxidation and absorption. These advantages reduce the initial plant investment by about 50 per cent.

From Sodium Nitrate



Reaction

$$NaNO_3 + H_2SO_4 \rightarrow HNO_3 + NaHSO_4$$

95–97% yield

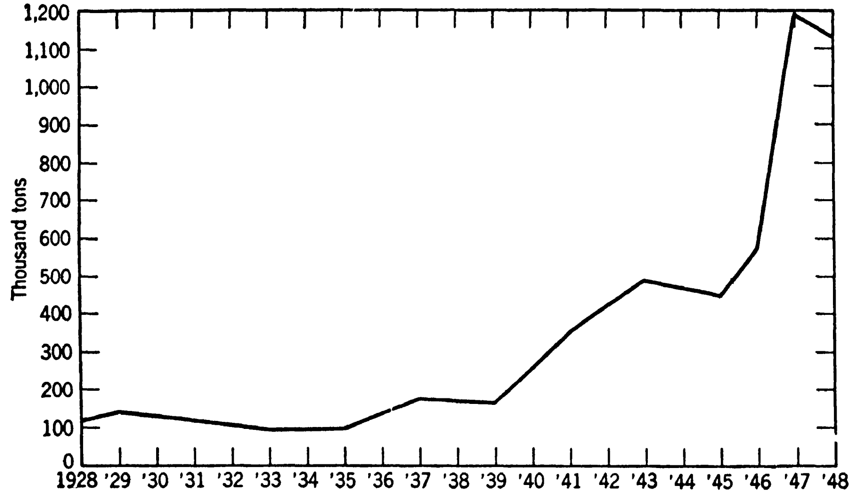
Material Requirements

Basis—1 ton nitric acid (100%)

Sodium nitrate (96%)	2,930 lb
Sulfuric acid (66°Bé)	3,150 lb

Process

Approximately equal parts of dried sodium nitrate and 66°Bé (93 per cent) sulfuric acid are charged batchwise to a direct-fired cast-iron retort, set in a brick housing. The firing of the retort plus the exothermic character of the reaction combine to heat the reactant mass to about 150 to 200°C for about 12 hr, during which time nitric acid, nitrogen oxides, and water distil off. The retort temperature is kept as low as possible because of the ease with which nitric acid is decomposed by heat. The nitric-acid vapors (110 to 130°C) are led through an acid-proof condenser, such as the Gutmann or the S-bend type, where they are cooled externally with water or internally with strong nitric acid to condense the acid vapors as concentrated nitric acid (96 to 99 per cent).



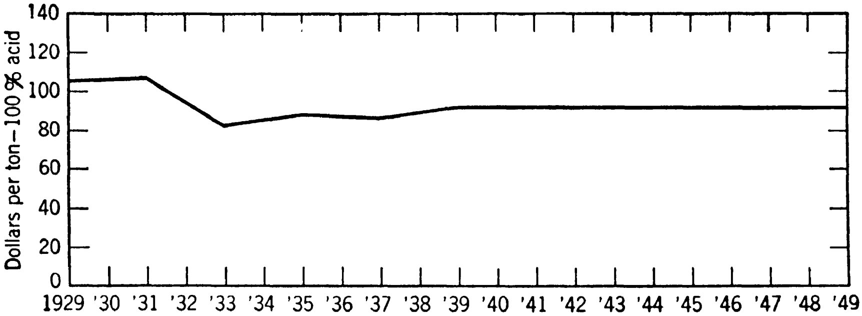
Production—Nitric Acid (100%)

Uncondensed vapors and oxides of nitrogen (consisting of 10 to 20 per cent of the nitric acid from the distillation) pass to a recovery system similar to the type described for the ammonia oxidation process. Since dissolved oxides of nitrogen impart a dark color to the product, a bleacher is used in conjunction with the recovery towers. Air is introduced into the bleacher and oxidizes the lower oxides to yield water-white nitric acid.

The residue remaining in the retort at the end of the 12-hr distillation contains sodium bisulfate and excess sulfuric acid and is called niter cake. This cake is withdrawn from the retort while still in the molten state and is allowed to solidify on acid-proof floors or is chilled on a flaker. The niter cake finds use in the heavy chemical and steel industries and for a long time has been employed as a raw material for hydrochloric-acid manufacture.

Use Pattern

	1947 (est.), per cent
Ammonium nitrate fertilizers	55
Explosives	25
Miscellaneous	20
	100



Price—Nitric Acid

Miscellaneous

Properties. Pure 100 per cent nitric acid is a colorless, highly corrosive liquid with powerful oxidizing properties. The commercial acid varies from colorless to a yellowish-red color, owing to the presence of dissolved nitrogen oxides.

Mol. wt.	63.02	M.P.	−42°C
Sp. gr.	1.502	B.P.	86°C, partial decomposition

Soluble in all proportions in water and forms a constant-boiling mixture at 760 mm pressure of 68 per cent acid and 32 per cent water with a boiling point of 110°C.

Solutions containing more than 86 per cent HNO_3 are known as fuming nitric acids.

Grades. Technical, 95 per cent or fuming, C.P., and USP (70 to 72 per cent, 1.42 sp. gr.). The technical or commercial grades are available in the following standard concentrations:

Degrees Baumé	Percentage HNO_3	Specific Gravity
36	52.3	1.330
38	56.5	1.355
40	61.4	1.381
42	67.2	1.408

Aqua Fortis is the name applied to the less pure all-purpose grade; it is available in the afore-mentioned concentrations.

In addition to the various grades of nitric acid, a nitrating or mixed acid (nitric acid, sulfuric acid, and water) is produced by nitric-acid manufacturers in the following standard proportions:

Nitric Acid, per cent	Sulfuric Acid, per cent
80	15
85	12
60	38
45	53

Containers and Regulations. Technical grades of weak acids (50 to 70 per cent), C.P., and USP (70 per cent) acids in glass carboys and bottles. Concentrated acid (95 per cent) in aluminum or stainless-steel drums and tank cars. Mixed acid (nitric and sulfuric) in iron drums or tank cars. A white ICC shipping label is required.

Economic Aspects

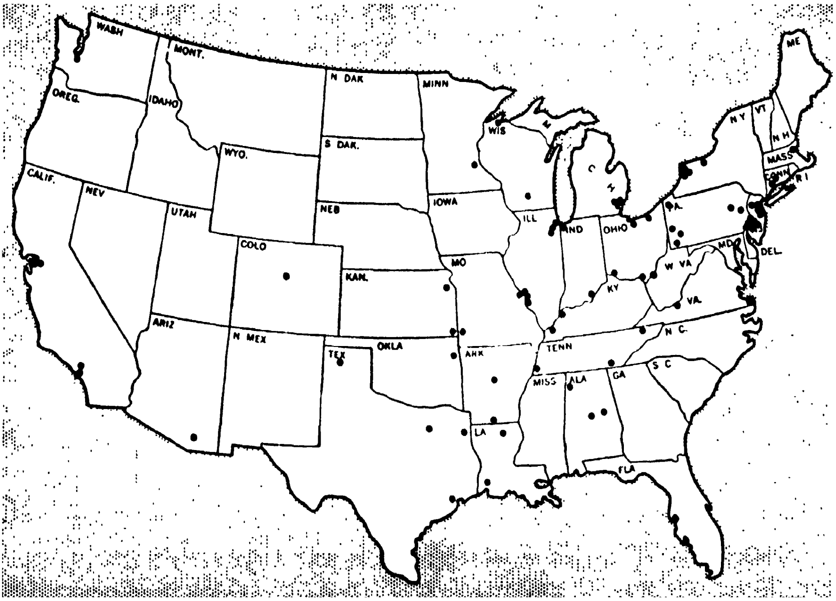
Nitric acid, unlike the other common acids, has a single large use, the manufacture of explosives. Consequently, in time of war, its production increases enormously. If, however, ammonium nitrate is accepted more widely for fertilizer use (a distinct possibility), and atomic energy becomes more important in future warfare, nitric-acid production may tend to level out.

Since over 90 per cent of the nitric acid used is made by the catalytic pressure oxidation of ammonia, and less than 10 per cent by the action of sulfuric acid on Chili saltpeter, there is a tendency for decentralized manufacture. Oxidation units may be quite small, and liquid ammonia may be shipped easily and cheaply, with the result that many users can afford to manufacture their own acid. Some of the older units are operated at atmospheric pressure, but pressure units (100 psi) are generally accepted as more economic. The capital cost of a pressure plant is half that of an atmospheric plant.

A third method of preparing nitric acid, which is of very little importance now, is the arc process. Nitrogen and oxygen of the air were made to combine when passed through an electric arc. The nitrogen oxides obtained were then converted to nitric acid. The acid obtained was only about 35 per cent HNO_3, and the power and investment costs were too high to offer serious competition to the other processes.

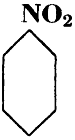
Considerable work was done during World War II on a process for the direct oxidation of nitrogen by passing air through a regenerative "pebble-bed" furnace, followed by quenching of the hot gases (3 per cent NO) and adsorption of the nitric oxide on a solid adsorbent. If refractory problems can be overcome (gas temperature reaches 4,000°F), the process may be economic under certain conditions.

Large production of nitric acid for sale is usually carried on by general heavy-chemical manufacturers or by synthetic-ammonia manufacturers. This type of plant might have a capacity of 10,000 to 40,000 annual tons. Such plants would consist of 3 to 8 units each with a daily capacity of 10 tons of nitric acid. Some of the more recent units have capacities of 45 tons per day each. A 25,000-ton plant costs about $100 per annual ton capacity.

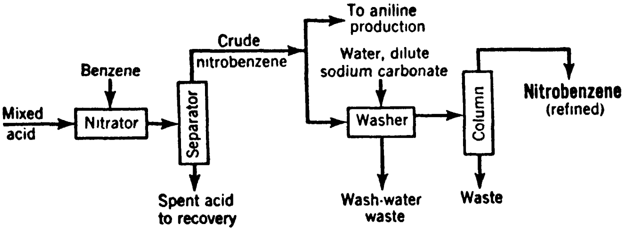


Location of Nitric-Acid Plants

NITROBENZENE



From Benzene and Nitric Acid



Reaction

$$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$$

95–98% yield

Material Requirements

Basis—1 ton nitrobenzene

Benzene		1,300 lb	Sodium carbonate	20 lb
Mixed acid	Sulfuric	1,442 lb		
	Nitric	1,060 lb		
	Water	218 lb		

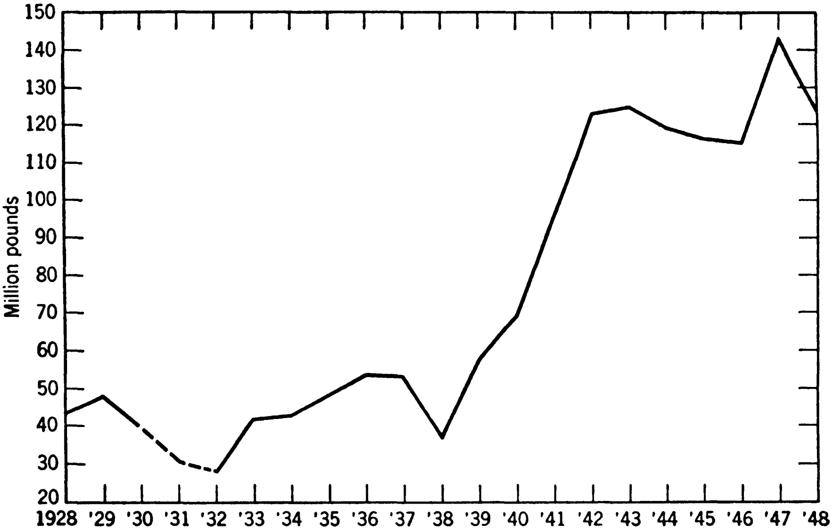
Process

Nitrobenzene is prepared by the direct nitration of benzene, using a nitric-acid–sulfuric-acid mixture. The reaction vessel or nitrator is a specially built cast-iron or steel kettle fitted with an efficient agitator. The kettle is jacketed and generally contains internal cooling coils for proper control of the exothermic reaction.

Benzene is charged to the nitrator. Mixed acid (composition approximately 60 to 53 per cent sulfuric acid, 32 to 39 per cent nitric acid, and 8 per cent water) is slowly added under the surface of the benzene. The temperature is maintained at 50 to 55°C by the rate of feed, agitator efficiency, and heat exchange. The ratio of reactants may be expressed several ways and varies from plant to plant. However, if a mixed acid of the afore-mentioned concentration is used, the weight ratio of mixed acid to benzene is about 2.5 to 1. The reaction time also varies but generally takes 2 to 4 hr. The temperature may be raised to about 90°C toward the end of the nitration.

The reaction mixture is run to a separator, where the spent acid separates and is drawn off the bottom. The spent acid is either recovered or used as cycle acid to start subsequent runs. The spent acid contains about 77 to 85 per cent sulfuric acid, 0 to 3 per cent nitric acid, and water.

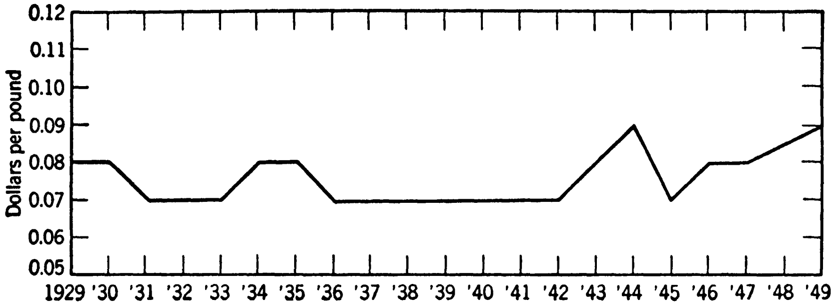
The crude nitrobenzene is drawn off the top of the separator and may be used directly for aniline manufacture. If a pure grade of nitrobenzene is desired, the crude material is sent to a washer, where it is washed with water, dilute sodium carbonate solution, and finally water again. It is then distilled to yield purified technical nitrobenzene. The yield based on the weight of benzene is about 95 to 98 per cent.



Production—Nitrobenzene

Use Pattern

	Per cent
Aniline	80
Miscellaneous	20
	100



Price—Nitrobenzene

Miscellaneous

Properties. Yellow crystals, or yellow oily liquid.

Mol. wt.	123.11	M.P.	5.7°C
Sp. gr.	1.205 18°C/4	B.P.	210.9°C

Weight per gallon 10 lb (25°C)

Soluble in alcohol, ether, and benzene. Very slightly soluble in water (0.2 per cent at room temperature).

Flash point (closed cup)	190°F
Ignition temperature	900°F
Vapor density (air = 1)	4.25

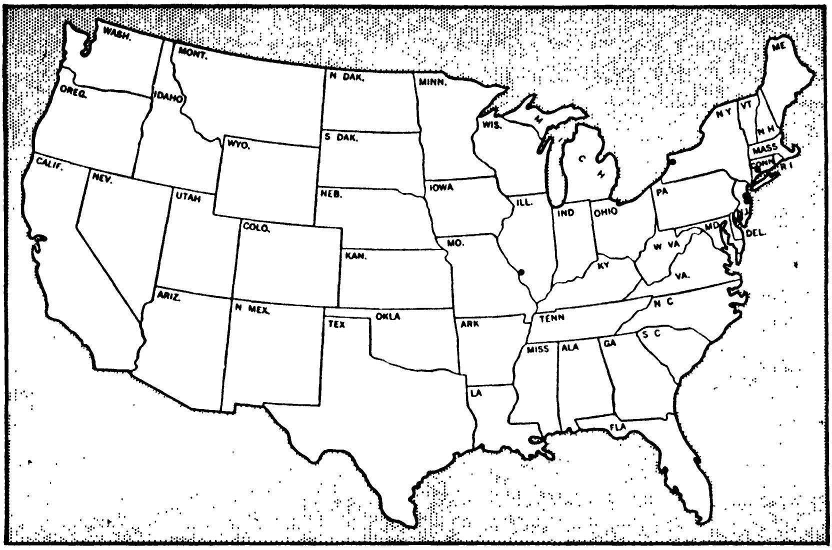
Grades. Technical, redistilled, and 97 per cent (oil of merbane).

Containers and Regulations. Tank cars, iron drums, tins, and bottles. Class B poison ICC shipping label required.

Economic Aspects

Nitrobenzene is one of the more important raw materials for the dye industry, and most nitrobenzene is used directly or indirectly (as aniline) in dye manufacture. It is usually manufactured either by dye manufacturers themselves or by companies supplying a variety of intermediates to dye manufacturers.

The benzene nitration process may be carried out on a comparatively small batch scale since the ratio of labor cost to raw-material cost is very low. It is estimated that 85 per cent of the manufacturing cost, which in this case includes charges on capital investment, may be attributed to raw materials. Modern nitrators, however, hold approximately a 1,000-gal charge of benzene, and operate on a 4-hr cycle. Operating procedures are directed toward maximum yield, because of the cost factors mentioned previously.

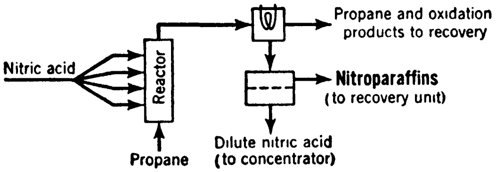


Location of Nitrobenzene Plants

NITROPARAFFINS

Nitromethane	CH_3NO_2
Nitroethane	$CH_3CH_2NO_2$
1-Nitropropane	$CH_3CH_2CH_2NO_2$
2-Nitropropane	$CH_3CHNO_2CH_3$

From Propane and Nitric Acid


Propane and oxidation products to recovery
Nitric acid
Reactor
Nitroparaffins (to recovery unit)
Dilute nitric acid (to concentrator)
Propane

Reaction

$$C_3H_8 + HNO_3 \rightarrow CH_3NO_2\ (10\%) + C_2H_5NO_2\ (25\%) + [C_2H_5NO_2CH_3 + C_3H_7NO_2]\ (65\%)$$

Material Requirements (Theoretical)

Basis—1 ton nitroparaffins (mixed)

Propane	1,070 lb
Nitric acid (100%)	1,530 lb

Process

The nitroparaffins are manufactured by the vapor-phase reaction of nitric acid and propane, or a lower-saturated hydrocarbon.

Propane, for example, is heated to 430 to 450°C and passed into an insulated reactor at 100 to 125 psi, where it comes into contact with a 75 per cent nitric-acid spray issuing from several nozzles along the length of the reactor. The sprays are so located and the amount of acid fed to each spray so controlled that the heat of vaporization of the acid counteracts the exothermic character of the reaction so that reaction temperature is maintained between 390 and 440°C. A sufficient number of stages is used so that the over-all molar ratio of propane to nitric acid is approximately 5 to 1. The ratio in any one stage is maintained at about 25 to 1. The reactor is constructed of stainless steel, and the inside wall is protected with a fused-silica or Pyrex-glass liner.

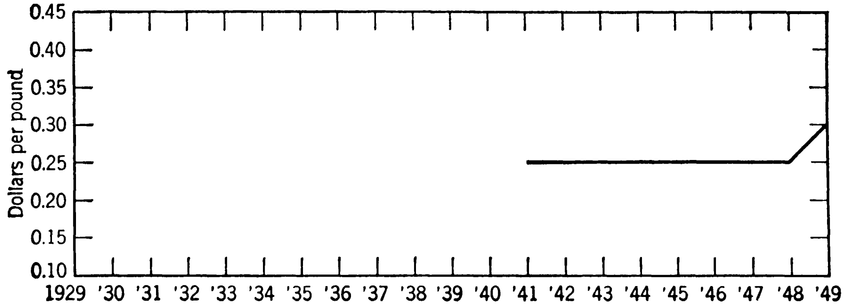
The gases issuing from the reactor are cooled, so that the nitroparaffin and dilute nitric acid are condensed. Propane vapors and gaseous oxidation products are sent to recovery units from which unreacted propane is recycled. The nitroparaffin layer in the separator is pumped to a series of stills for fractionation into its various constituents. The dilute nitric-acid layer is used as make-up for further nitrations.

Production

No data available.

Use Pattern

Chemical intermediate Solvent	No breakdown available



Price—Nitromethane

Miscellaneous

Properties. *Nitromethane* (CH_3NO_2). Colorless liquid.

Mol. wt.	61.04	M.P.	−28.5°C
Sp. gr.	1.138 20°C/20	B.P.	101°C

Weight per gallon 9.5 lb. (20°C)

Soluble in alcohol and ether. Soluble in water (9.5 ml per 100 ml at 20°C). Water is soluble in nitromethane (2.2 ml per 100 ml at 20°C).

Flash point (open cup)	112°F
Vapor density (air = 1)	2.11

Nitroethane ($C_2H_5NO_2$). Colorless liquid.

Mol. wt.	75.07		
Sp. gr.	1.052 20°C/20	B.P.	114.0°C

Weight per gallon 8.75 lb (20°C)

Soluble in alcohol and ether. Slightly soluble in water (4.5 ml per 100 ml at 20°C). Water is soluble in nitroethane (0.9 ml per 100 ml at 20°C).

Flash point	106°F

1-*Nitropropane* ($CH_3CH_2CH_2NO_2$). Colorless liquid.

Mol. wt.	89.09		
Sp. gr.	1.003 20°C/20	B.P.	132.0°C
Weight per gallon	8.35 lb (20°C)		

Soluble in alcohol and ether. Slightly soluble in water (1.4 ml per 100 ml at 20°C).

Flash point	120°F

2-*Nitropropane* ($CH_3CHNO_2CH_3$). Colorless liquid.

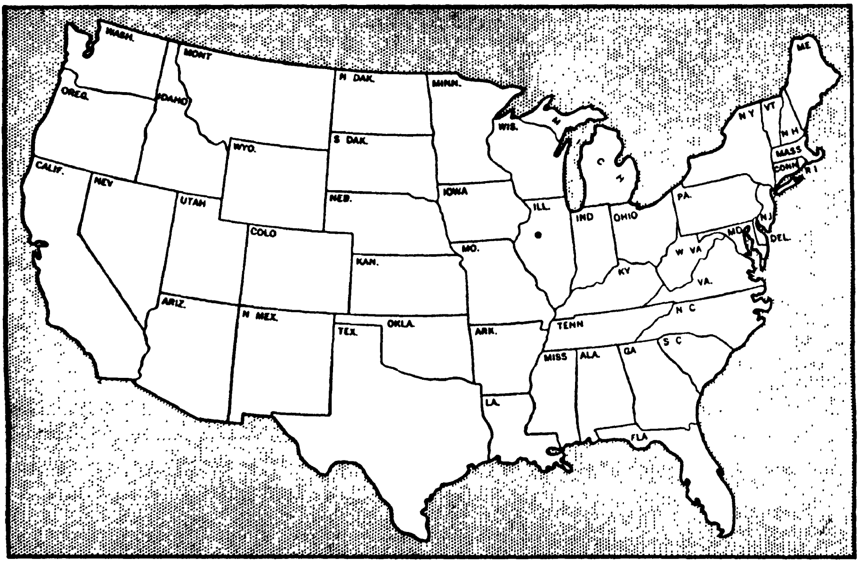
Mol. wt.	89.09		
Sp. gr.	0.992 20°C/20	B.P.	120.3°C
Weight per gallon	8.24 lb (20°C)		

Soluble in alcohol and ether. Slightly soluble in water (1.7 ml per 100 ml at 20°C).

Flash point	103°F

Grades. Technical.

Containers and Regulations. Drums, cans, and bottles. No ICC shipping label required.



Location of Nitroparaffin Plant

Economic Aspects

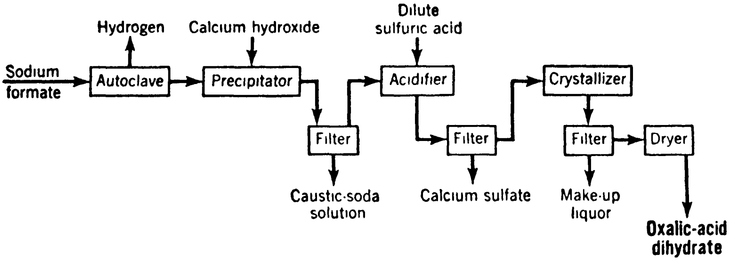
The nitroparaffins (nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane) were first produced commercially in 1937. Accordingly, as would be expected, markets for these products are only partially developed. A large number of derivatives have been synthesized and are being evaluated in a variety of synthetic-organic-chemical reactions. The first uses developed were naturally solvent uses, but these uses too have not been completely explored. This group of nitroparaffins is interesting to chemists, however, and will undoubtedly find a secure place in the American chemical industry. One possible large use for nitromethane may develop in rocket fuels.

Production is only by one company. Data on economic plant size and investment are not available, although reports are current that the company contemplates the construction of a new plant with an annual capacity of 15,000 tons of nitroparaffins.

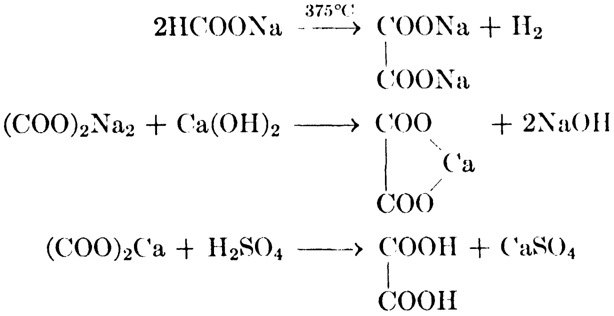
OXALIC ACID

$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array}$$

From Sodium Formate



Reaction



$$2\mathrm{HCOONa} \xrightarrow{375°\mathrm{C}} \begin{array}{l}\mathrm{COONa}\\ |\\ \mathrm{COONa}\end{array} + \mathrm{H_2}$$

$$(\mathrm{COO})_2\mathrm{Na_2} + \mathrm{Ca(OH)_2} \longrightarrow \begin{array}{l}\mathrm{COO}\diagdown\\ |\qquad\ \mathrm{Ca}\\ \mathrm{COO}\diagup\end{array} + 2\mathrm{NaOH}$$

$$(\mathrm{COO})_2\mathrm{Ca} + \mathrm{H_2SO_4} \longrightarrow \begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array} + \mathrm{CaSO_4}$$

80–90% yield

Material Requirements

Basis—1 ton oxalic-acid dihydrate

Sodium formate	2,700 lb
Calcium hydroxide	1,340 lb
Sulfuric acid (100%)	1,925 lb

Process

Sodium formate is produced by the reaction of solid sodium hydroxide (97 to 98 per cent) and carbon monoxide at 200°C and 150 psi in an autoclave. See *Formic Acid* for details.

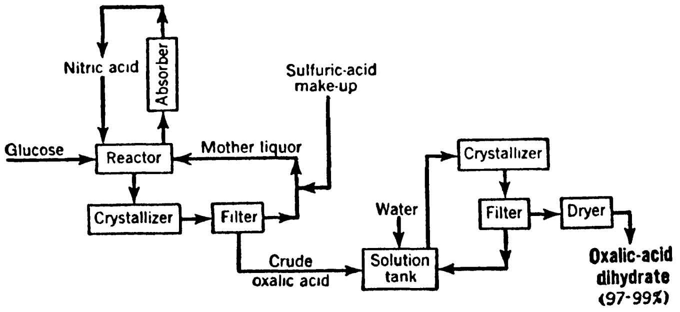
After the reaction is completed, the pressure is reduced in the autoclave, and the temperature is raised to 375°C. The sodium formate is converted into sodium oxalate, and the hydrogen formed is exhausted from the autoclave. When the evolution of hydrogen has ceased, the reaction is complete.

The reaction mixture (crude sodium oxalate) is transferred to a precipitator, where calcium hydroxide is added with thorough agitation. The calcium oxalate formed is filtered off, and the sodium hydroxide solution is concentrated for re-use. The filter cake, containing crude sodium oxalate plus small amounts of calcium carbonate, is run to an acidifier, where it is reacted with dilute sulfuric acid. A large percentage of the calcium precipitates out as calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$). The solution is concentrated, precipitating more calcium sulfate, which is filtered off.

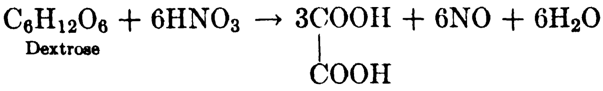
The mother liquor is run to a crystallizer, where it is concentrated to a gravity of 30°Bé and cooled. Oxalic acid crystallizes out in the form of the dihydrate ($HOOCCOOH \cdot 2H_2O$), which is washed and dried. The mother liquor is re-used as make-up in subsequent batches. The yield of oxalic-acid dihydrate is about 80 per cent by weight based on sodium formate. It is generally sold and used as the dihydrate, but anhydrous oxalic acid may be formed by heating the dihydrate to 100°C where it loses 2 molecules of water.

The sodium oxalate formed in the autoclave may be acidified directly to oxalic acid by mixing 1 part of sodium oxalate with 3 parts of methanol. To this slurry is added 0.8 part of concentrated sulfuric acid. After thorough agitation, insoluble sodium sulfate separates from the methyl oxalate–methanol–sulfuric-acid solution. The sodium sulfate is filtered off, and the mother liquor is hydrolyzed by the addition of 3.5 parts of water. Oxalic acid and methanol are formed. The latter is distilled for re-use. The crude oxalic-acid residue is concentrated and the oxalic acid crystallized.

From Carbohydrates



Reaction



$$\underset{\text{Dextrose}}{C_6H_{12}O_6} + 6HNO_3 \rightarrow 3\begin{array}{c}COOH\\ |\\ COOH\end{array} + 6NO + 6H_2O$$

60–70% yield (starch)

Material Requirements

Basis—1 ton oxalic-acid dihydrate

Glucose (60%)	2,112 lb
Nitric acid (90%)	5,153 lb
Sulfuric acid (100%)	116 lb

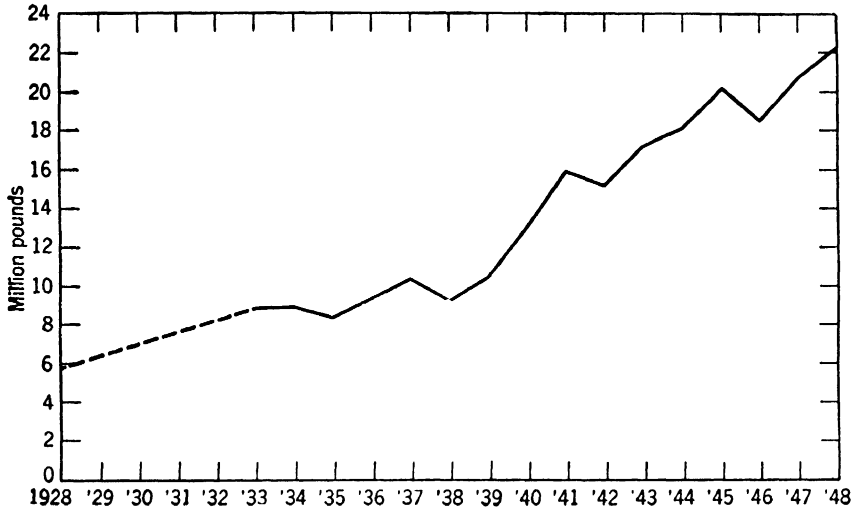
Process

Oxalic acid is prepared by the oxidation of carbohydrates such as glucose, sucrose, starch, dextrin, and cellulose by nitric acid. The alkali (potassium and sodium hydroxides) fusion of carbohydrates also yields oxalic acid. The fusion method is particularly applicable in the utilization of waste cellulosic materials, such as sawdust, corn cobs, cornstalks, and oat hulls.

Raw starch (85 per cent) is dispersed by slurrying it in approximately an equal amount of 11 per cent oxalic-acid solution at 167 to 176°F. After refluxing for approximately 6 hr, virtually all the starch is hydrolyzed to a monosaccharide, chiefly glucose. The hydrolyzed starch solution, containing about 60 per cent glucose (monosaccharide), is mixed with oxalic-acid mother liquor recovered from the filtration step of the previous run. This mother liquor is enriched with small amounts of sulfuric acid and catalysts to compensate for process losses: that is, 1 to 2 per cent of 100 per cent sulfuric acid based on the weight of the recovered mother liquor. The adjusted mother-liquor solution contains approximately 50 per cent sulfuric acid, 5 per cent oxalic acid, 0.5 per cent ferric iron (as ferric sulfate), and 0.005 per cent vanadium (as vanadium pentoxide). The glucose–mother-liquor solution is heated to about 160°F with good agitation in a reactor. Nitric acid of 65 to 95 per cent strength is gradually added at a rate suited to maintain the temperature at 160°F. Some external cooling is generally used to facilitate the acid addition. The ratio of the glucose (60 per cent) solution–nitric-acid (90 per cent)–mother-liquor solution (50 per cent sulfuric acid) is approximately 1 to 2.5 to 7.5. Oxides of nitrogen evolved during the reaction are absorbed in a suitable nitric-acid absorption system. The nitric-acid product from the system is concentrated for re-use.

When the oxidation is completed, the solution is run into a crystallizer, where it is cooled (75 to 90°F) with agitation. The resulting slurry is filtered, and the mother liquor is recycled for subsequent runs. The crude oxalic-acid filter cake contains about 90 per cent oxalic-acid dihydrate which may be dried. The yield is about 1.65 parts of oxalic acid per part of raw starch: that is, approximately 70 per cent of the total starch is converted to the acid.

Oxalic acid of higher purity may be obtained by dissolving the crude product in an equal weight of water at 150°F. After the solution is cooled to about 75°F, the slurry is filtered, and the mother liquor is returned to the dissolving tank. The filter cake is dried below 150°F, and the resulting oxalic-acid dihydrate ($HOOCCOOH \cdot 2H_2O$) assays 97 to 99 per cent.



Production—Oxalic Acid

Oxalic acid may also be obtained by the direct action of nitric acid on corn cobs, oat hulls, sawdust, and other cellulosic materials. One part by weight of ground corn cobs, oat hulls, or sawdust is added to 3 parts by weight of cold 95 per cent nitric acid. After the initial reaction has moderated, the mass is heated to dissolve the cellulose. The mixture is cooled, and 0.1 per cent vanadium pentoxide and 3 parts (based on the original weight of the corn cobs or oat hulls) of 50 to 55 per cent nitric acid are added. The mixture is allowed to stand several days at room temperature to complete the oxalic-acid formation and crystallization.

The nitrogen oxides evolved are absorbed and reconverted to concentrated nitric acid. The crystals of oxalic acid are filtered and purified, as described previously. The mother liquor is circulated through the absorption system, where the nitrous acid is converted to nitric acid for re-use. The average yield of oxalic-acid dihydrate is about 1 ton of acid per ton of corn cobs and 1.1 to 1.2 tons of acid per ton of oat hulls.

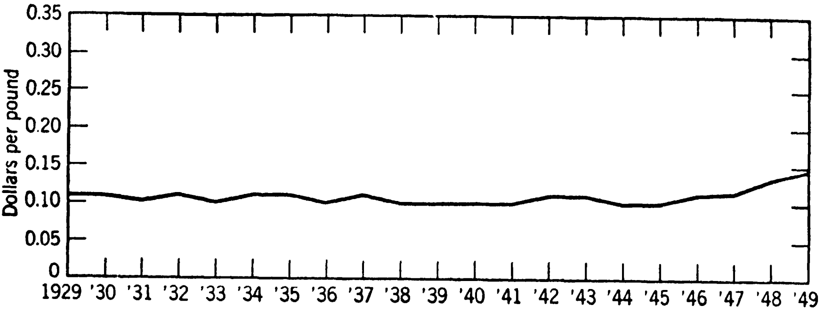
The alkali fusion of carbohydrates yields oxalic acid plus other organic acids such as acetic acid. The general procedure is to mix sawdust or corn cobs with about 2.5 to 3.0 times their weight of sodium hydroxide plus a small amount of water. The mixture is slowly heated to a temperature of 400 to 475°F. The lemon-yellow fusion mass is cooled and then lixiviated. The resulting oxalate salt is neutralized with sulfuric acid. The yield of oxalic-acid dihydrate is 25 to 35 per cent based on the weight of oat hulls, cornstalks, corn cobs, or sawdust. About 15 to 25 per cent volatile acids are also obtained. These comprise acetic acid (12 to 18 per cent) and formic acid (3 to 10 per cent).

Oxalic acid is also produced by fermentation of sugar. See *Citric Acid.*

Use Pattern

Laundries (acid rinse)
Leather tanning and manufacture
Chemical processing
Bleaching agent
Photography
Medicinals
Dyes and inks

No breakdown available



Price—Oxalic Acid

Miscellaneous

Properties. Anhydrous (HOOCCOOH)—colorless, odorless monoclinic crystals or white powder with a marked acid taste.

Mol. wt.	90.04	M.P.	186 to 187°C, with decomposition
Sp. gr.	1.90	B.P.	Sublimes at 100°C

It crystallizes from water as the dihydrate ($HOOCCOOH \cdot 2H_2O$) in the form of colorless monoclinic prisms with the following properties:

Mol. wt.	126.07	M.P.	101.5°C
Sp. gr.	1.653 19°C/4	B.P.	Loses $2H_2O$ at 100°C

Soluble in water (10 g per 100 ml at 20°C, 120 g per 100 ml at 100°C), absolute alcohol (24 g per 100 g at 15°C), and ether (1.3 g per 100 g at 15°C).

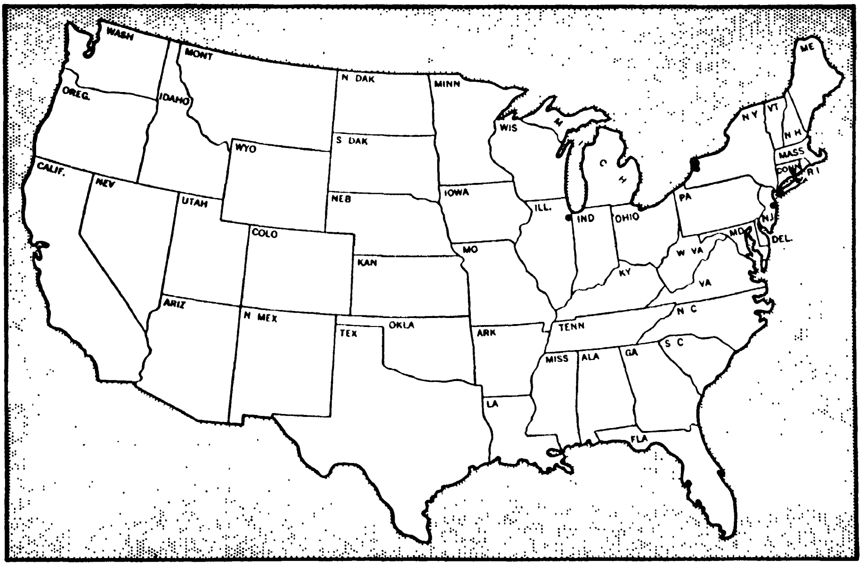
Grades. Technical (crystals and powder) and C.P. Both grades are the dihydrate (containing 2 molecules of water).

Containers and Regulations. Barrels, casks, kegs, boxes, cans, and bottles. Oxalic acid is considered a poisonous substance and is hazardous if the vapors or dusts are inhaled or contacted with the skin and mucous membranes. A fatal dose (taken internally) varies from 0.5 to 1 oz. No ICC shipping label required.

Economic Aspects

Oxalic acid may in a sense be considered a joint product with formic acid, since a slight change in process variables in the most widely used process may give either material as a product.

Some manufacturers, however, still find it advantageous to manufacture oxalic acid by the action of caustic soda on sawdust (the process is rapidly disappearing) or of nitric acid on sucrose, dextrose, or other



Location of Oxalic-Acid Plants

carbohydrate material. The competitive situation appears to depend on raw-material cost and supply in a given plant and on the other products manufactured by the company. Although the starch hydrolyzate–nitric-acid oxidation process described previously makes use of oxalic acid in the starch hydrolysis, the usual practice is to hydrolyze the starch with sulfuric or muriatic acid and then oxidize the resulting hydrolyzate. By far the larger share of production, however, is made by the carbon monoxide–caustic-soda process. Oxalic acid is also obtained as a by-product of citric-acid manufacture in the fermentation process for the latter (see *Citric Acid*).

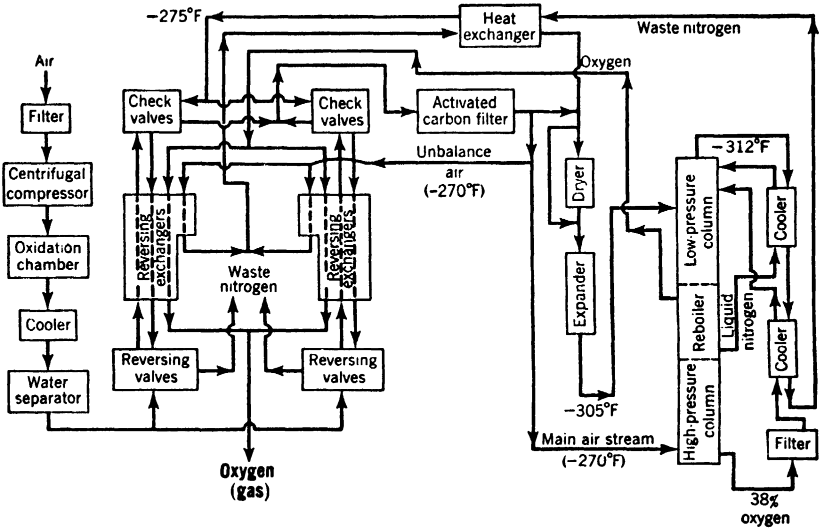
The uses for oxalic acid center around its calcium-ion removal and reducing properties. Thus, it is used widely as a laundry "sour," as a bleach for removing iron stains from a variety of materials, and in cleaning compounds. Further gradual utilization of these properties may be expected in the future, rather than large sudden increased use.

A 1,000,000-lb-per-yr plant, using the nitric-acid oxidation process, costs about $60,000, chiefly for nitric-acid-recovery equipment.

OXYGEN

O_2

From Air by Liquefaction (Modified Linde-Frankl Cycle)



Recovery

90% recovery

Material and Utility Requirements

Basis—1 ton 90% oxygen (350-ton-per-day plant) (or 23,450 cu ft)

Air (standard conditions)	123,200 cu ft
Steam (800 psi, 800°F)	3,325 lb
Cooling water	1,000 gal
Electricity	350–400 kw-hr

Process

Commercial oxygen is produced in two grades (high purity 99.5 per cent, and low purity 90 to 98 per cent) by the liquefaction and subsequent fractionation of air. A number of different cycles have been proposed. These vary in methods of air compression, purification, and refrigeration, as well as in the design of heat-exchange, rectifying, evaporating, and condensing equipment. The pressures of the various cycles range from about 60 to 3,000 psi.

Air consists of an invariable mixture of gases, as indicated by the following volume percentages: 78.03 per cent nitrogen, 20.99 per cent oxygen, 0.94 per cent argon, 0.01 per cent hydrogen, and smaller amounts of neon, helium, krypton, and xenon. It also contains variable concentrations of carbon dioxide (0.03 to 0.07 per cent by volume), water vapor (0.01 to 0.02 per cent), and hydrocarbon gases such as acetylene.

In the modified Linde-Frankl low-pressure cycle, reversing exchangers are used to lower the temperature of the incoming air, which flows countercurrent to the outgoing gas. Critical cooling is obtained by the Joule-Thompson effect: that is, the cooling effect produced by expansion of compressed air with no external work (1 kg of air at 3,000 psi and 10°C, when expanded to 75 psi, produces a cooling effect of 10 kg-cal).

Air is filtered and compressed to 77 psi in a two-stage steam-driven centrifugal compressor and then passed through a catalytic oxidation chamber. Here traces of hydrocarbons such as acetylene are converted to carbon dioxide and water. After cooling, the hydrocarbon-free air is passed through a water separator and then to automatic three-way reversing valves, which select the proper air channels through the exchangers. The exchangers, which function both to cool and to purify the air, have a concentric, triple-tube construction in which the oxygen product follows the same path through the center tube, while waste nitrogen and incoming air switch channels in the two outer annuli. This periodic switching (about every 3 min) enables the carbon dioxide and water vapor, which condense from the incoming high-pressure air, to be evaporated and purged out of the system by the low-pressure waste nitrogen.

The high-pressure air entering the exchangers is saturated with water at about 90°F and 77 psi. It also contains approximately 0.03 mole per cent carbon dioxide. As the air is cooled, it progressively deposits first water, then ice, and finally carbon dioxide snow. Leaving the top of the last exchanger through automatic check valves and at a temperature of -270°F, the cold purified air passes through activated carbon filters, which remove any remaining carbonaceous impurities. The air stream is then divided into three portions; part of the air, called the "unbalanced" stream, is returned to an extra jacket at the top of the exchangers where it is warmed to about -120°F, passed through a heat exchanger against waste nitrogen, and then blended with a second portion of the air stream to give a mix temperature of −244°F. The air stream may be passed through silica-gel dryers and then fed into a turboexpander.

The "temperature unbalance" system of diverting a part of the air stream introduces a small amount of refrigeration into the reversing exchangers to compensate for heat losses. It also gives the necessary cold-end temperature difference (5°F) to permit constant low exchanger-outlet temperatures and insures complete purging of impurities, thereby giving excellent air purification. The silica-gel dryer is used, when starting up the cycle, to remove water contained in the as yet unpurified air. The turboexpander supplies the refrigeration for the whole unit. In it the air at −244°F and 77 psi is expanded through nozzles against a high-speed turbine, which is connected to an electric generator. The air leaves the turbine at its dew point, −305°F and 7.5 psi, and is fed into the upper section of a double-fractionating column.

The third and main portion of the air stream, at a temperature of −270°F, enters the bottom of the double column. In the high-pressure section, operating at 71.5 psi, the air is condensed, and preliminary fractionation takes place. The more volatile nitrogen (B.P. −320.5°F, −195.8°C, or 77.3°K) rises to the top of the high-pressure section, where it is condensed in a condenser-reboiler by heat exchange with boiling oxygen in the low-pressure section of the column. The nitrogen, about 94 per cent pure, serves as reflux to the trays in the high-pressure section and is then withdrawn from the column. After passing through a subcooler where the temperature is reduced by heat exchange with the overhead waste nitrogen stream from the low-pressure section, the liquid nitrogen at about 71 psi is expanded through a valve near the top of the low-pressure column to 7 psi. Here it serves as reflux to the top tray of this section, giving up some of its oxygen and forming the waste-nitrogen exhaust.

At the base of the column, so-called rich liquid air, containing about 38 per cent of the less volatile oxygen (B.P. −297.4°F, −183°C, or 90.1°K), is removed and passed through a glass-cloth filter to remove any traces of precipitated carbon dioxide. It is then cooled in a subcooler against the waste nitrogen gas and fed through an expansion valve at an intermediate point in the low-pressure (7-psi) section of the column. Here it is further fractionated to give oxygen of desired purity and waste nitrogen. Reboiler heat is furnished at the bottom of the top section by the condensation of nitrogen at the top of the bottom (high-pressure) section. The nitrogen in the top section vaporizes and passes upwards through the liquid reflux, which scrubs, to some extent, the oxygen out of the feed stream to give an oxygen yield as high as 90 per cent.

The number of trays in the column depends on the purity and yield of oxygen desired. For 90 to 95 per cent oxygen, most of the argon remains in the product, and fractionation takes place between oxygen and nitrogen. For making high-purity (99.5 per cent) oxygen, fractionation must take place between argon (B.P. −302.3°F, −185.7°C, or 87.2°K) and oxygen, which is more difficult and requires more high-capacity high-efficiency trays.

Part of the oxygen product may be withdrawn as liquid, although in this type of low-pressure cycle most of it is withdrawn as vapor at −292°F from the vapor space below the bottom tray in the top section of the column. It is returned through the reversing exchangers where it is warmed to substantially inlet temperature (90°F).

The waste nitrogen leaves the top of the column at −312°F and is used to subcool both the nitrogen reflux and the rich air feed. It is then returned through the heat exchanger, where it cools the "unbalance" air and passes to the main reversing exchangers. It enters these at a temperature of −275°F and a pressure of 7 psi and is reheated to within 7°F of the entering air. After the impurities of carbon dioxide and water released by the incoming air are removed, the waste nitrogen is exhausted into the atmosphere.

The process part of the plant is enclosed by a steel section surrounding the various pieces of equipment. All the void spaces are filled with mineral wool, thus affording the required insulation. The units are of necessity particularly tight and leak-free and are usually constructed of nonferrous metals such as copper, aluminum, and high-chrome–nickel alloys.

Conventional Linde-Frankl Cycle

The other low-pressure process for making oxygen, the conventional Linde-Frankl cycle, differs essentially from the foregoing in its use of "cold accumulators" for purification and heat transfer. These are pressure vessels (operating at about 70 psi) packed with aluminum spirals in which both waste-nitrogen and oxygen product cool the incoming air by a periodic reversal of the flow. Since the oxygen product purges the impurities, this process produces only low-purity oxygen. A second difference is in the use of a small amount (4 to 5 per cent) of high-pressure (3,000-psi) supplementary air to make up refrigeration deficiencies. The supplementary air also aids in purging the "accumulators," being used in place of the "unbalance" air stream employed by the previously described process.

Other Cycles

Other methods for producing oxygen from air operate at moderate to high pressures and, in general, follow the basic Linde or Claude cycles. Most plants rely on chemical methods for removing carbon dioxide, and some employ chemicals also for water removal. Alkalies such as sodium or potassium hydroxide may be used for both, or sodium hydroxide for carbon dioxide removal and silica gel for water. Water is often separated from the air stream, however, by freezing in an exchanger and removing with waste nitrogen or warm refrigerant gas.

In the Linde cycle with auxiliary refrigeration, the air is compressed as high as 3,000 psi, scrubbed with a sodium hydroxide solution, and cooled in alternating heat exchangers against product oxygen and nitrogen. At 5°F most of the water is frozen out, and the air is further cooled to −50°F in a second pair of alternating exchangers against refrigerated ammonia. The cold purified air is then fractionated in a double column to yield oxygen and nitrogen.

Claude Cycle

The basic Claude cycle operates at a lower pressure (about 400 psi) than the Linde cycle but is similar in the method of air purification. The novel feature is passing up to 80 per cent of the main air stream through an expansion machine. By this adiabatic expansion, the power consumption per unit of air is reduced by about 35 per cent. After the air has expanded to do work, it is combined with the rest of the air, which has been allowed to expand for self-refrigeration, and passed into a fractionator.

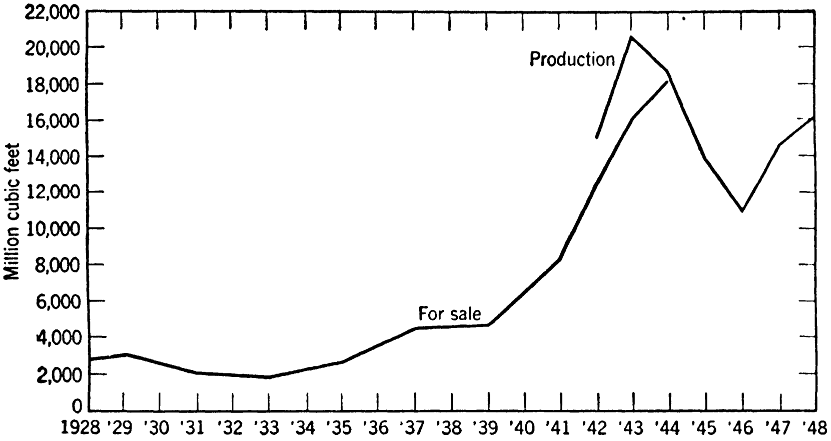
One modification of the Claude cycle used in large plants consists of compressing filtered air, scrubbing with caustic, and drying with activated alumina or silica gel. While the air is cooling in exchangers against outgoing oxygen and nitrogen, part of it is taken off and put through a reciprocating expansion engine. The other part of the air, after completing the heat-exchange cooling, is expanded from 750 psi operating pressure to column pressure. It is combined with the air from the expander and fractionated in a double column to produce liquid oxygen, which is discharged at cylinder-filling pressure.

A further modification is the Heylandt cycle, which claims a still lower power consumption (30 per cent less) by using high pressure (3,000 psi) and introducing about 60 per cent of the air to the expander at room temperature (rather than at 190°F as in the Claude cycle). The remaining 40 per cent is throttled.

By using any of these cycles or various modifications, it is possible to produce liquid or gaseous oxygen ranging in purity from about 90 to

99.5 per cent. The liquid is withdrawn directly from the column, or, if gaseous oxygen is desired, it may be stored in a gas holder and then compressed prior to cylinder filling. The nitrogen, produced as a coproduct, may be recovered or vented to the atmosphere. The rare gases may also be separated by additional fractionation. Plants separating these gases obtain an argon fraction (boiling between oxygen and nitrogen) and may process the nitrogen gas to obtain a neon–helium fraction (lower boiling than nitrogen). By special processing of liquid oxygen, a krypton–xenon fraction (higher boiling than oxygen) may be obtained.

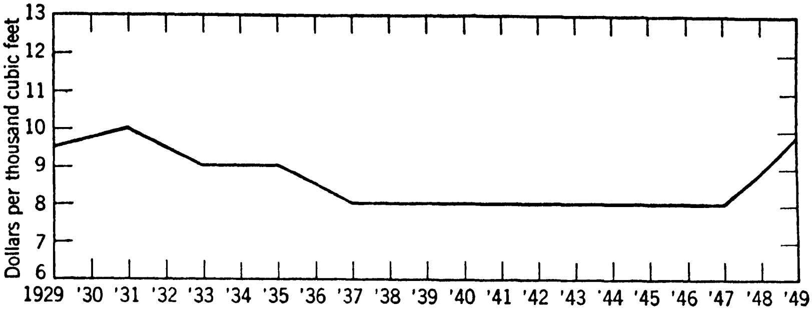
Oxygen is also produced in minor quantities as a coproduct with hydrogen in the electrolysis of water. For details, see *Hydrogen.*



Production—Oxygen

Use Pattern

	1947 (est.), per cent
Cutting and welding	90
Other	10
	100



Price—Oxygen (Cylinders: contract, small lots. As much as 67% off for large quantities—200 tons per month)

Miscellaneous

Properties. Colorless, odorless, tasteless gas liquefiable at −190°C into a slightly bluish liquid.

Mol. wt.	32.00	M.P.	−218.8°C
Sp. gr.		B.P.	−183°C
Gas	1.1053 (air = 1)		
Liquid	1.14 (−183°C)		
Solid	1.426 (−252.5°C)		

Slightly soluble in water (4.89 cc per 100 g at 0°C, 2.6 cc per 100 g at 30°C, 1.7 cc per 100 g at 100°C), and alcohol.

Grades. Technical, pure, and USP (99.5 to 99.9 per cent). Lower grades (90 to 95 per cent) made and consumed on premises.

Containers and Regulations. Seamless steel cylinders (usually holding 220 cu ft (18.2 lb) and 110 cu ft (9.1 lb) under 2,000 psi, and gas bottles. Green (gas) ICC shipping label required.

Economic Aspects

Approximately 97 per cent of the oxygen produced in the United States is made by the liquefaction of air and subsequent fractional distillation. The remainder is electrolytic oxygen. In liquefaction processes most of the by-product nitrogen is wasted; in the electrolytic process more oxygen is made than is consumed, since the cells are operated primarily for hydrogen production. In either case, cheaper oxygen is obtained with complete utilization of the other product made.

Conventional liquefaction processes vary primarily in the method of cooling the air to be liquefied and in the pressure used. In general, small plants must use higher operating pressures than large ones. In certain large installations the rare gases, neon, argon, krypton, and xenon, are recovered and purified. The demand for these inert gases for fluorescent and display lighting has increased enormously in the last 10 years.

Oxygen-manufacturing units vary in size from small electrolytic units to large liquefaction units that may have capacities as high as 3,000,000,000 cu ft per yr. Most commercial plants, however, vary in size from 30,000,000 cu ft to 100,000,000 cu ft annual production. In certain locations, small liquefaction plants with annual capacities between 1,500,000 and 10,000,000 cu ft are economical.

Large complete plants will cost about $5,000 per 1,000,000 cu ft annual capacity. Small plants are much more expensive. Until several years ago, nearly all oxygen made in the United States was made by three large companies who could afford extensive research on production economics and new uses.

During World War II, however, marked progress was made in the design and application of turbocompressors and turboexpanders. These units made possible considerable savings in investment and operating costs of large (so-called tonnage oxygen) plants. These savings, in addition to those inherent in producing lower-purity (90 to 95 per cent) oxygen instead of the standard 99.5 per cent grade, have led to a tremendous change in the outlook for cheap oxygen on a large scale.

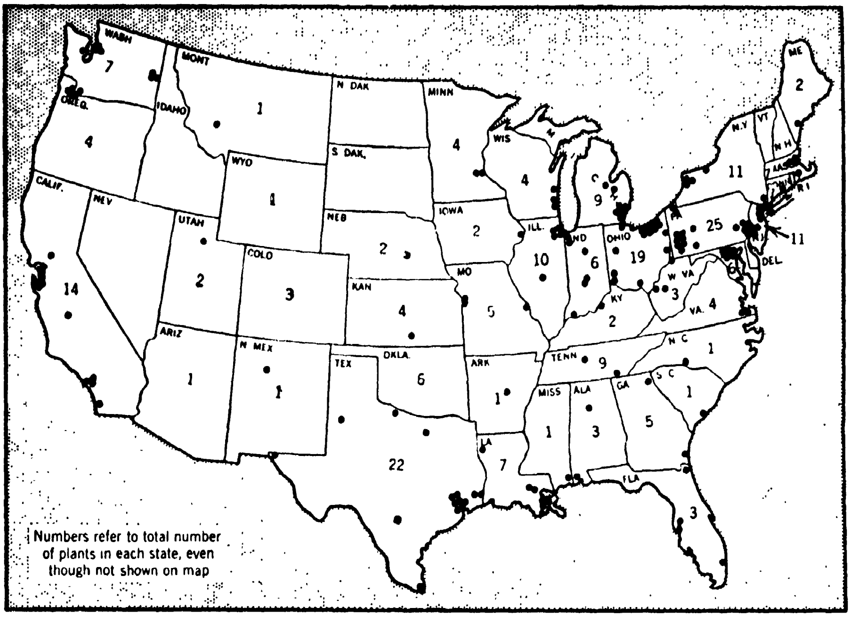
Several plants for the production of 90 to 95 per cent oxygen have recently been built or are under construction. Their capacities range from 135 tons per day (850,000,000 cu ft per yr) to two 1,000 ton-per-day units (each over 6,000,000,000 cu ft per yr) in a single plant. This plant was built in conjunction with a hydrocarbon-synthesis plant, utilizing a modified Fischer–Tropsch (Synthol) process. The other tonnage oxygen plants will be used in conjunction with iron and steel plants, for either open-hearth or blast-furnace operations.

Many technical men expect comparatively large-scale utilization of cheap low-purity oxygen in various oxidation processes, such as coal gasification, water-gas synthesis, and oxidation of ammonia to nitric acid. In various organic oxidation processes, oxygen-enriched air appears to be feasible if oxygen costs can be lowered. It has even been predicted that the technology of sulfuric-acid manufacture may be seriously affected by the use of oxygen-enriched air in the burning of sulfur-containing raw materials. Chlorine production may also be affected, if the oxidation of by-product hydrochloric acid to chlorine becomes a reality.

It has been estimated that plants producing 90 to 95 per cent pure oxygen in the range of 150 to 750 tons per day will cost $3,500 to $7,500 per ton daily capacity, depending on size.

One company is offering small high-purity oxygen generators based on the Linde-Frankl system, in sizes ranging from 200 to 10,000 cu ft per hr. In many cases, cylinder oxygen has been used on this scale.

In a small oxygen plant equipment cost is important. In a large one power cost is most important. It has been estimated that power cost must be less than 5 mills per kw-hr.

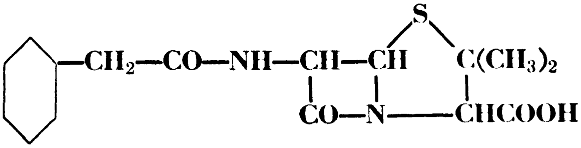


Numbers refer to total number of plants in each state, even though not shown on map

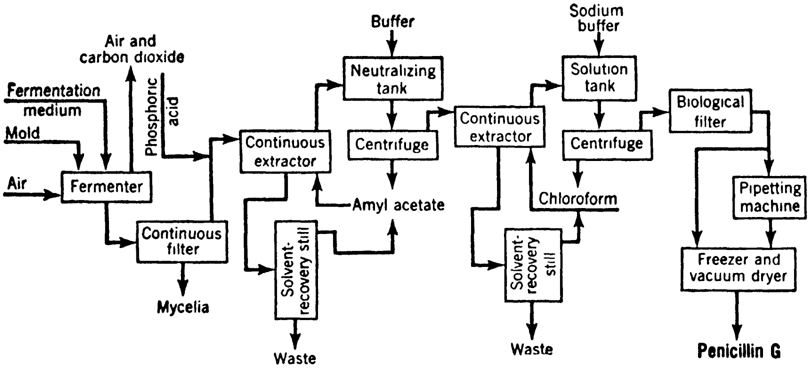
Location of Oxygen Plants

PENICILLIN

(PENICILLIN G)



By Deep-Tank Fermentation



Recovery

50–70% (from beer)

Material Requirements

Basis—100,000,000 Oxford units (*ca.* 0.132 lb) penicillin

Corn-steep liquor (dry basis)	17.5 lb	Mold spore preparation	1.5 gal
Lactose	17.5 lb	Water	50 gal
Calcium carbonate	4.5 lb	Air	15,000 cu ft
Nutrients	Variable	Amyl acetate, chloroform	Variable, losses only
Added organic chemicals	Variable		

Process

Under specific conditions, a suitable fermentation medium is inoculated with selected mold spores, which multiply, producing penicillin. When the fermentation has reached the optimum stage, the mold is filtered off, and the clear liquor is extracted to yield a purified solution of penicillin, which is then dried to the final powdered product.

Corn-steep liquor, a by-product of the corn wet milling industry, serves as the basic fermentation medium. It is diluted with water to the proper concentration, adjusted in *p*H with calcium carbonate, and fortified with lactose and small quantities of nutrient salts, such as magnesium sulfate, zinc sulfate, potassium dihydrogen phosphate, and sodium nitrate. Various organic chemicals are usually added to the medium to increase the total yield and to modify the type of penicillin produced: for example, the production of penicillin G is aided by the addition of a precursor such as phenyl acetic acid. The amounts of nutrients and alkali added, as well as the degree of dilution, vary from plant to plant and depend to a great extent on the quality of the corn-steep liquor used. A typical aqueous medium may be said to contain about 4 per cent corn-steep solids, 4 per cent lactose, 1 per cent calcium carbonate, and small amounts of nutrient salts and organic chemicals.

The aqueous culture medium, adjusted to a *p*H of approximately 5.5, is charged into carbon-steel fermentation tanks ranging in capacity from 1,000 to 15,000 gal. A typical 5,000-gal fermenter consists of a vertical steam-pressure vessel (Inconel-clad) equipped with heating and cooling coils, a turbine-type agitator, and a sparger for introduction of air. The fermentation medium is sterilized by heating to about 15 lb steam pressure for ½ hr. The tank is then cooled by introducing cooling water into the coils.

When the 5,000 gal of fermentation medium has reached a temperature of about 75°F (24°C), it is inoculated under aseptic conditions by the introduction of 150 gal of mold spores. The mold is previously prepared by breeding a selected strain of *Penicillium chrysogenum* or *Penicillium notatum* on agar slants in the media laboratory and germination in seed tanks.

To start the fermentation cycle, the medium is agitated at a constant speed, and sterile air is blown through the tank via the sparger at a rate of at least 400 cu ft per min. Frothing is minimized by adding an antifoam agent such as octadecanol, and the temperature (75°F) is maintained constant by the circulation of cooling water through the coils. The aerobic mold is allowed to grow 48 to 72 hr, during which time carbon dioxide is evolved.

When the optimum amount of penicillin has formed, as determined by assay, the fermented liquor (containing large quantities of mycelia and relatively small amounts of penicillin) is passed through a stainless-steel heat exchanger, where it is cooled to about 28°F (2°C). It is then run through a stainless-steel rotary vacuum filter where the mycelia are removed and discarded. The clear filtrate, known as beer, contains 500 to 1,000 Oxford units of penicillin per milliliter and has a purity of about 10 units per milligram dry weight.

The penicillin is recovered from the crude liquor by either continuous-countercurrent solvent extraction or a combination of adsorption and batch extraction. Both processes are similar in principle and serve to separate, concentrate, and purify the product. The newer direct-extraction method has virtually replaced all the processes based on activated carbon adsorption.

In the continuous-extraction process, the *p*H of the crude broth (beer) is adjusted to about 2.5 with dilute (10 per cent) phosphoric acid. The liquor is then passed into continuous extractors, where the penicillin is extracted by amyl acetate. The raffinate, containing the water-soluble impurities and some of the solvent, is sent to a solvent-recovery system. The penicillin-containing extract is run to a neutralizing tank where a buffer solution of disodium phosphate and sodium acid phosphate is added. Penicillin passes into the buffer solution, which is separated from the amyl acetate by a supercentrifuge. The solvent is recovered for re-use.

The aqueous buffer solution of penicillin is acidified and passed into a second series of continuous extractors, where it passes countercurrent to chloroform. The penicillin goes into solution in chloroform; the raffinate is sent to solvent-recovery units. The extract is then agitated with a pyrogen-free distilled-water solution of sodium hydroxide or a buffered sodium bicarbonate–phosphate solution. Depending on the end product desired, a source of calcium ions may be used in place of the sodium salt. The sodium (or calcium) salt of penicillin formed readily dissolves in water; separation of the immiscible liquids is accomplished by supercentrifuging. By these extraction operations, the penicillin in the contents (5,000 gal) of the fermenter is concentrated to approximately 50 gal of solution, about a hundredfold reduction of the original volume.

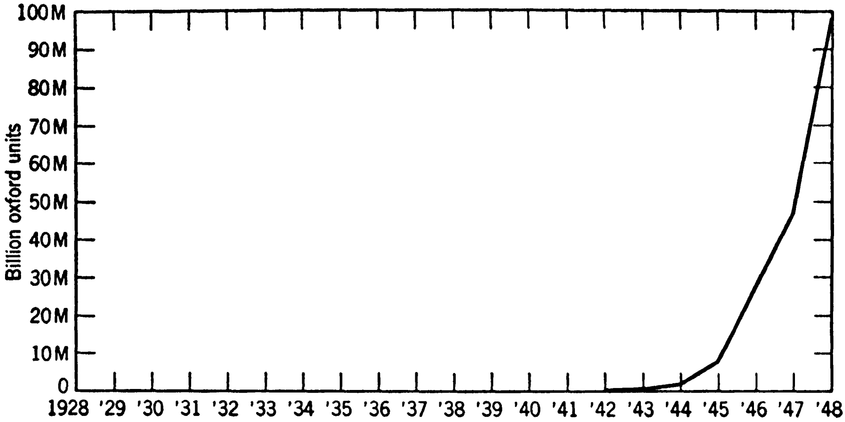
In the adsorption method, the crude filtered liquor from the fermenters is pumped into closed, agitator-equipped stainless-steel tanks. Here it is mixed with 2 to 2.5 per cent of its weight of activated carbon. After about ½ hr, the carbon slurry is filtered on a centrifuge or filter press, and the spent beer is discarded. The penicillin-containing carbon filter cake is washed on the press and then charged into an elution tank where the penicillin is eluted with 80 per cent aqueous acetone. The charcoal is removed by filtration and sent to a reactivation system. The crude penicillin in the filtrate has a purity of about 100 units per milligram dry weight and represents an over-all recovery at this point of 60 to 70 per cent of that present in the original fermentation liquor.

The penicillin-rich acetone is then concentrated by a three-stage vacuum-spray evaporator. Operating at a top temperature of 65°F and at pressures of 3, 1, and <1 in. of mercury, in each stage, respectively, the acetone is removed until the liquor leaving the third stage is about 99.5 per cent water and penicillin. The aqueous concentrate is adjusted with phosphoric acid to a *p*H of about 2.5 and then extracted batchwise with amyl acetate, followed by chloroform at a temperature of 28°F.

The extract is treated with aqueous alkali to form the water-soluble salt and fed to a flash concentrator of the circulating type operating at 40°F and a pressure of 0.1 in. Hg. The penicillin, which is now purified to about 950 units per milligram (dry basis), is discharged from the centrifugal separator. By the adsorption-extraction batch method, the original 5,000-gal batch has diminished to about 5 gal. Commercial penicillin produced usually contains about 80 per cent penicillin G. The concentrated and purified water solution of penicillin is blown through a biological plate-and-frame filter to remove any bacteria or pyrogens present. The resulting sterile solution is then dried in bulk or in final containers under aseptic conditions designed to eliminate any chance of contamination. This may be done by lyophilization (freeze drying), vacuum-spray drying, or electronic drying. The lyophilizing procedure consists of freezing the sodium (or calcium) penicillin solution and dehydrating at low temperature by sublimation through high-vacuum (less than 1 mm mercury), multijet diffusion pumps. Electric-radiant heaters, mounted under the shelves holding the vials or bulk material in the freeze dryers, supply the latent heat of evaporation of ice and maintain the temperature at about −4°F (−20°C). Since dry penicillin is relatively stable, the temperature toward the end of the drying cycle is allowed to rise and thus remove residual moisture.

The electronic-drying system, using a 2,000-watt radio-frequency generator, operates in three stages. In the first, at 50°F, the bulk is reduced in about 30 min by dehydrating at a rate of 3 l per hr. The solution may be then charged into vials where, in a vacuum dryer employing electronic heat, 1-ml quantities of concentrated penicillin solution are reduced to the dry state in about 3 min while the vials rotate at 3,000 rpm. The final stage uses moderate-vacuum heating chambers where, for a period of 30 min, last traces of moisture are removed from the dried products.

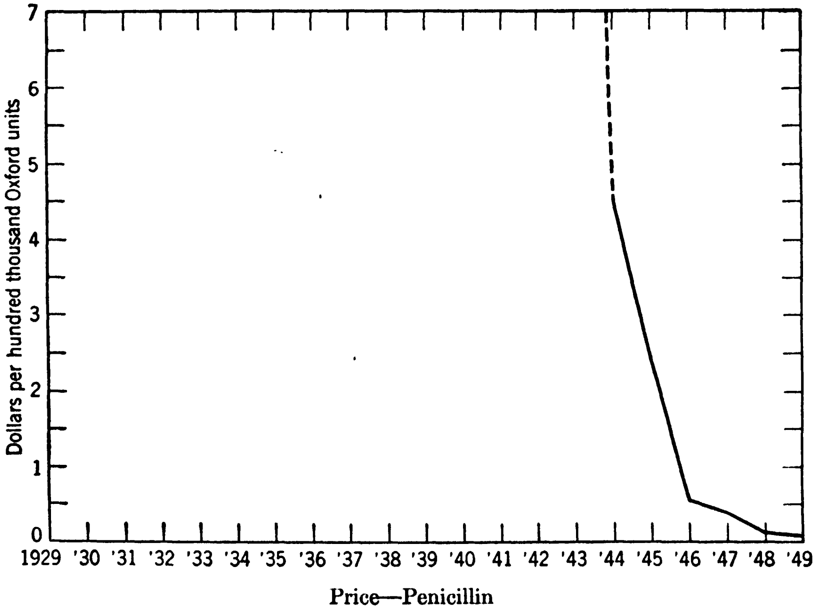
In the preparation of crystalline penicillin, the concentrated water solution of penicillin as it comes from the biological filter, or after it has been further concentrated by passage through a bulk reducer, serves as the starting material. Several methods of obtaining crystals have been patented and, in general, involve adding a neutral salt such as ammonium sulfate to the solution until it becomes turbid. The penicillin is allowed to crystallize out on standing. Further purification is carried out by recrystallization from organic solvents. Usually another organic liquid having less solvent action on penicillin is added to the solution to facilitate crystallization. A further method of purification leading to crystalline sodium penicillin makes use of a magnesium trisilicate chromatogram. The penicillin G produced by crystallization has a high purity, ranging from 1,500 to 1,600 units per milligram.



Production—Penicillin

Use Pattern

Medicinal 100 per cent

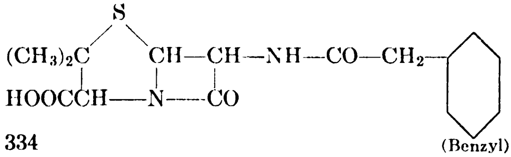


Price—Penicillin

Miscellaneous

Properties. Penicillin, a mixture of organic acids of complicated structure, is usually isolated as the sodium or calcium salt. At least five types of penicillin showing antibiotic activity have been obtained by fermentation methods. Although penicillin G normally constitutes about 80 per cent of the regular fermentation product, it is possible to produce various yields of the other known penicillinic acids. The five types of penicillin currently identified are as follows:

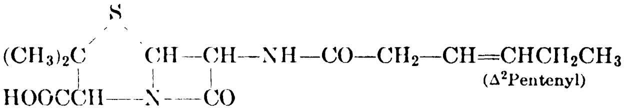
Penicillin G



Mol. wt. 334

Activity 1,667 Oxford units per milligram (standard) *

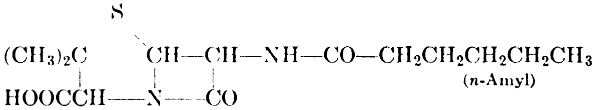
Penicillin F



Mol. wt. 312

Activity 1,550 Oxford units per milligram

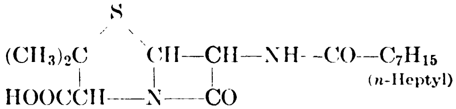
Penicillin dihydro F



Mol. wt. 314

Activity 1,700–1,900 Oxford units per milligram

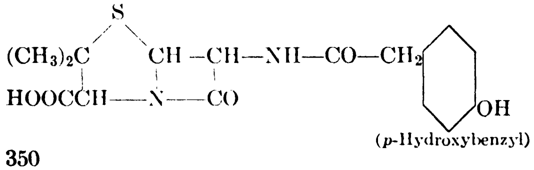
Penicillin K



Mol. wt. 342

Activity 2,300 Oxford units per milligram

Penicillin X



Mol. wt. 350

Activity 900 Oxford units per milligram

* As a standard, the activity of pure penicillin G against staphylococcus aureus *in vitro* has arbitrarily been set at 1,667 units per milligram. Other activities are relative.

Grades. Calcium penicillin, USP, amorphous; potassium penicillin, crystalline; procaine penicillin (penicillin G, calcium, sodium, or potassium, in oil), also amorphous; sodium penicillin, USP, both amorphous and crystalline.

Penicillin is available in a number of different forms to meet the physician's requirements for administration. Parenteral types for intravenous or intramuscular injection are amorphous sodium penicillin, crystalline sodium penicillin, and calcium penicillin. Intramuscular administration also employs penicillin in oil and beeswax. Other forms include penicillin tablets (tableted with starch and an antiacid) and penicillin capsules in oil for oral administration; penicillin troches and dental cones (tableted with sugar) for local oral use; penicillin ointment and creams for topical application; and inhalators.

Containers and Regulations. Sodium penicillin (amorphous and crystalline) and calcium penicillin are generally packaged in bulk or in vials containing 100,000 to 1,000,000 Oxford units and up. Penicillin in oil and wax is packaged in 5- to 10-cc vials containing 100,000 to 300,000 units per cubic centimeter. Crystalline sodium penicillin in dry state may be stored at room temperature, whereas the other forms require refrigeration during storage. The FDA certifies all penicillin produced and has issued monographs regulating the potency and purity.

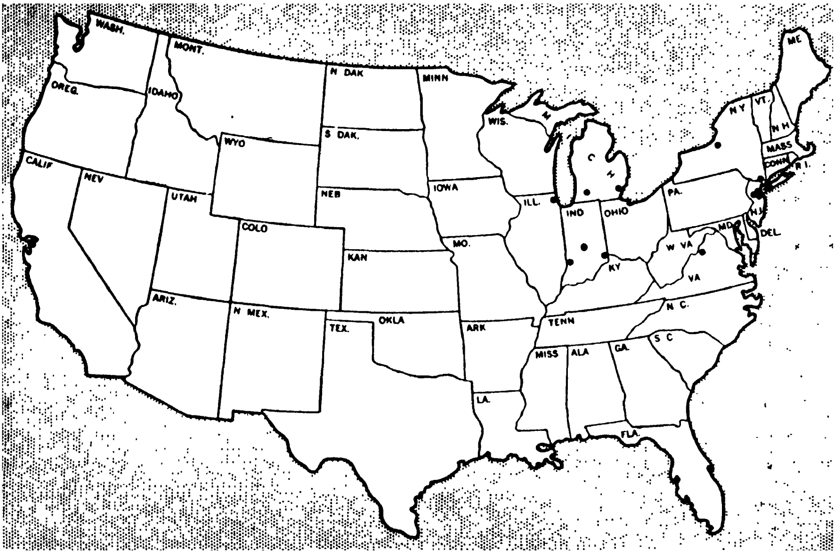
Economic Aspects

Penicillin has been termed the "wonder drug," and certainly during World War II it earned its name in saving the lives of many wounded soldiers. The value of the drug in controlling infections was transmitted to American scientists by the British in 1941 and early 1942. Commercial production began in 1943, although experimental quantities were manufactured on a large laboratory scale in 1942. The first commercial plants produced penicillin by surface fermentation in glass bottles, but the submerged fermentation process was developed shortly thereafter and soon became standard practice.

In the wartime scramble to build new plants, a large number of companies erected facilities, but it is interesting to note that those reaching maximum production first were those with broad experience in industrial fermentations. Early yields were very low but increased markedly during the war, because of the development of more efficient processing methods and new strains of mold. Considerable research was done during the war on a method of synthesizing penicillin, but to date an economic process has not been developed.

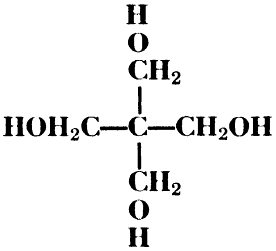
Although perhaps not the "wonder drug" or "cure all" it has been popularly thought to be, penicillin has become an important medicinal and shows promise of even greater use. Since 1947 production has been of greater total annual value than any other fermentation product, including ethyl alcohol.

Since the war various other antibiotics, of greater specificity to particular disease organisms, have appeared on the market. These other antibiotics, principally streptomycin, aureomycin, chloromycetin (chloramphenicol), and bacitracin, have supplemented penicillin, however, rather than replaced it. On the other hand, penicillin has definitely affected sulfa-drug production, which is currently only 30 per cent of the 1943 peak.



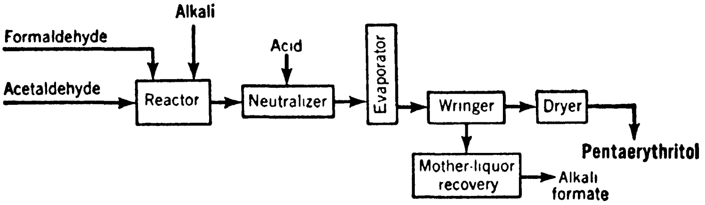
Location of Penicillin Plants

PENTAERYTHRITOL



$$\begin{array}{c} \mathrm{H} \\ \mathrm{O} \\ \mathrm{CH_2} \\ | \\ \mathrm{HOH_2C{-}C{-}CH_2OH} \\ | \\ \mathrm{CH_2} \\ \mathrm{O} \\ \mathrm{H} \end{array}$$

From Formaldehyde and Acetaldehyde



Reaction

$$4HCHO + CH_3CHO + NaOH\ [\text{or } Ca(OH)_2] \rightarrow$$

$$C(CH_2OH)_4 + HCOONa\ [\text{or } (HCOO)_2Ca]$$

80–90% yield

Material Requirements

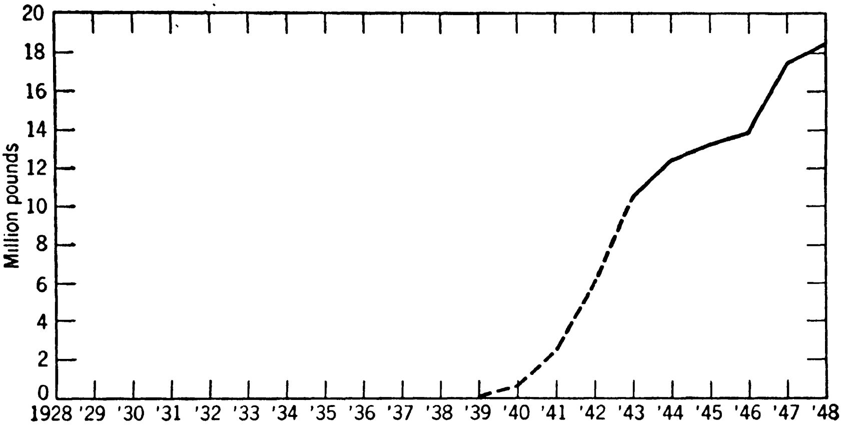
Basis—1 ton pentaerythritol

Formaldehyde (37%)	6,350 lb	Alkali (50%)	2,100 lb
Acetaldehyde	765 lb	Acid (as formic)	1,200 lb

Process

To a solution of formaldehyde (20 to 30 per cent by weight) is added either 50 per cent sodium hydroxide solution or 50 to 80 per cent calcium hydroxide slurry while the temperature is maintained at 15 to 20°C. With suitable agitation, 99 per cent liquid acetaldehyde is slowly added under the surface of the formaldehyde–alkali solution. Since the reaction is exothermic, external cooling is used to maintain the reaction temperature between 20 and 25°C. The mole ratio of formaldehyde to acetaldehyde generally used is between 4.5 to 1 and 5.0 to 1. A ratio of 1.0 to 1.5 moles of hydroxyl ion per mole of acetaldehyde appears to be the optimum amount of condensing agent. The temperature of the reaction mixture is held at 25 to 30°C for several hours and is then raised to about 60°C until the free aldehyde content is less than 0.1 per cent.

The crude reaction mixture is transferred to the neutralizing tank, where an acid is added to neutralize the excess alkali and to effect removal of the metallic ion of the condensing agent. If sodium hydroxide is used, formic acid may be added to reduce the pH of the solution to 7.8 to 8.0 and subsequently to remove the sodium ion present as sodium formate. If calcium hydroxide is the condensing agent, sulfuric acid or oxalic acid, either alone or conjunctively, may be employed to precipitate the calcium ion as calcium sulfate and calcium oxalate. The calcium salt is removed by filtration.



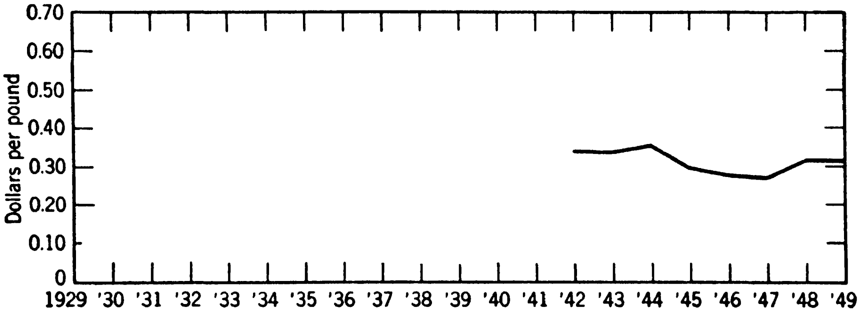
Production—Pentaerythritol

The solution is then evaporated to a specific gravity of about 1.270. It is chilled to crystallize pentaerythritol, and the resulting slurry is filtered. The mother liquor goes to a recovery system where it is reworked. If sodium hydroxide acted as the condensing agent, the sodium ion is removed as sodium formate during this operation. If the calcium process is used, the calcium ion is removed in the previous step by filtration.

The filter cake contains pentaerythritol and polypentaerythritols. The latter material is formed by side reactions and is a mixture of ether-linked polymers such as dipentaerythritol, $(CH_2OH)_3CCH_2—O—CH_2C(CH_2OH)_3$, and tripentaerythritol, $(CH_2OH)_3CCH_2—O—CH_2C(CH_2OH)_2CH_2—O—CH_2C(CH_2OH)_3$. Other by-products found in the reaction liquors include both linear and cyclic formals of the various pentaerythritols. The amounts of these polypentaerythritols and formals formed vary with reaction procedures and may be kept at a minimum under proper reaction conditions. The filter cake may be dried to yield technical pentaerythritol, or it may be purified by conventional methods such as crystallization to yield purified pentaerythritol, which is suitable for nitration purposes. The yield of pentaerythritol plus polypentaerythritols is about 85 to 90 per cent by weight based on the acetaldehyde charged.

Use Pattern

	1948 (est.), per cent
Resins, plastics, and drying oils	98
Other	2
	100



Price—Pentaerythritol

Miscellaneous

Properties. Colorless crystals or white crystalline powder. Pentaerythritol is odorless, sweet tasting, neutral, and nonhygroscopic.

Mol. wt.	136.15	M.P.	260°C
Sp. gr.	1.399 25°C/4	B.P.	276°C (30 mm) sublimes

Combining weight (number of weight units required to equal one hydroxyl group) is 34.0, and all hydroxyl groups are esterifiable. Sublimes slowly with some decomposition at about 130°C at high vacuum.

SOLUBILITY

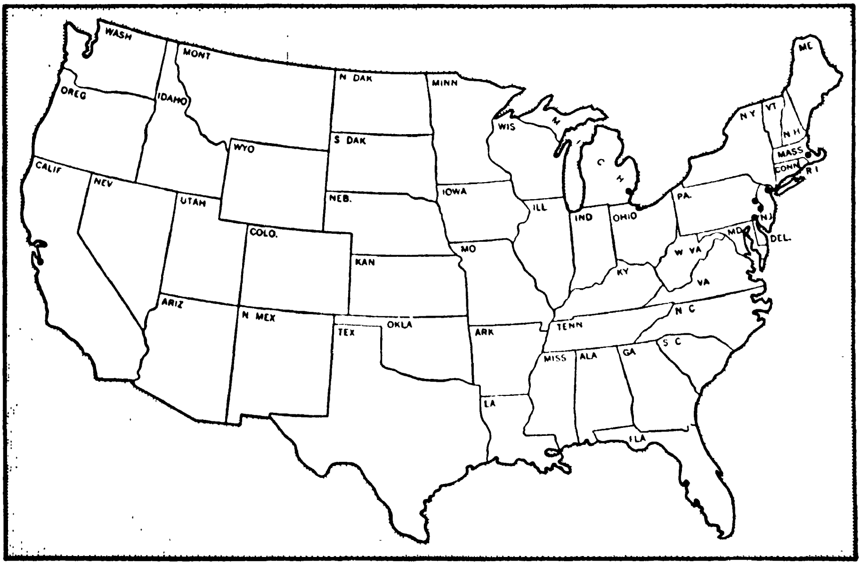
Water at 25°C	6.5 g in 100 g solvent
Water at 100°C	90 g in 100 g solvent
Ethanol at 25°C	0.5 g in 100 g solvent
Glycerol at 100°C	10.3 g in 100 g solvent
Diethylene glycol at 100°C	7.7 g in 100 g solvent
Formamide at 100°C	21.3 g in 100 g solvent
Acetone	Insoluble
Benzene	Insoluble
Paraffin	Insoluble
Carbon tetrachloride	Insoluble
Ether	Insoluble
Oils and fats	Insoluble

Grades. Technical (contains about 85 to 90 per cent pentaerythritol and 15 to 10 per cent related solid polyhydric alcohols such as dipentaerythritol), and purified (*ca.* 99 per cent).

Containers and Regulations. Purified: barrels and fiber drums (300 lb). Technical: barrels (250, 200 lb), fiber drums (100 lb), paper bags (75 lb), and bottles. Pentaerythritol is apparently nontoxic and nonirritating to the skin. No ICC shipping label required.

Economic Aspects

Pentaerythritol (PE) production increased markedly during World War II as a raw material for the explosive, PETN (pentaerythritol



Location of Pentaerythritol Plants

tetranitrate). The latter was used chiefly as a booster for TNT to produce a powerful explosive charge.

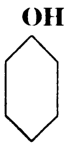
Pentaerythritol in a peacetime market competes with other polyhydric alcohols, chiefly in the resin field and in the upgrading of drying oils. Pentaerythritol–maleic anhydride resins have shown characteristics that may lead to very wide use.

Considerable PE production during the war came from Ordnance plants, but a number of private plants were also operated. Capacities of these plants vary generally from 1,000,000 to 10,000,000 lb per yr. The cost of such plants is approximately $150,000 per 1,000,000 lb annual capacity.

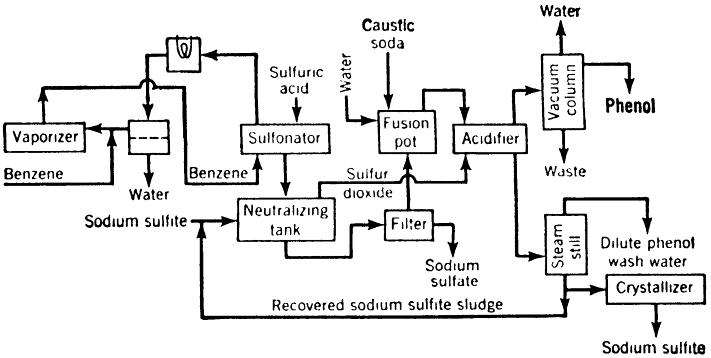
Manufacturers also making acetaldehyde or formaldehyde have a margin over others in the manufacture of PE, but those manufacturing other synthetic-resin raw materials also have a place in the field. The chief variation in processes, if the patent literature is any indication, is in the purification of the reaction mass.

PHENOL

(CARBOLIC ACID)



Benzenesulfonate Process



Reaction

$$C_6H_6 + H_2SO_4 \longrightarrow C_6H_5SO_3H + H_2O$$

$$2C_6H_5SO_3H + Na_2SO_3 \longrightarrow$$

$$2C_6H_5SO_3Na + SO_2 + H_2O\ (+\ Na_2SO_4)$$

$$C_6H_5SO_3Na + 2NaOH \longrightarrow C_6H_5ONa + Na_2SO_3 + H_2O$$

$$2C_6H_5ONa + SO_2 + H_2O \xrightarrow{H_2SO_4} 2C_6H_5OH + Na_2SO_3\ (+\ Na_2SO_4)$$

85–90% yield

Material and Utility Requirements

Basis—1 ton phenol

Benzene	2,000 lb	Steam	4,000 lb
Sulfuric acid (66°Bé)	3,500 lb	Electricity	80 kw-hr
Caustic soda	3,400 lb		

Process

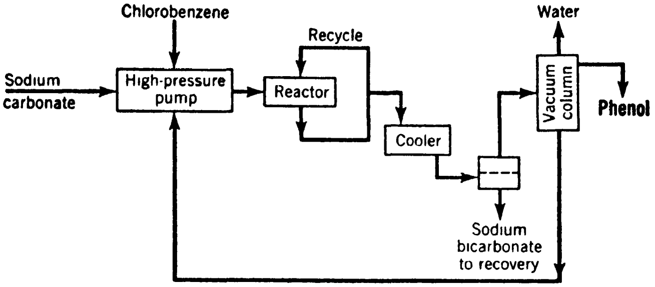
Benzenesulfonic acid is prepared in a sulfonator by the action of concentrated sulfuric acid on benzene. Water is formed during the reaction and must be removed because of its diluting effect on the acid. When the concentration of the sulfuric acid drops below 78 per cent H_2SO_4, the sulfonating action ceases. In order to circumvent this, the sulfonation is carried out continuously in the vapor phase by passing benzene vapors up through a reaction zone countercurrent to concentrated (66°Bé) sulfuric acid. The benzene reacts with the acid and also azeotropically removes the water of reaction. The reaction zone is maintained at an approximate temperature of 150°C. The sulfonation proceeds until only a few per cent of free sulfuric acid remains, which is then directly neutralized in the neutralizing tank. The benzene, water, and acid vapors are condensed, and the benzene is recovered.

The sulfonation product is added as rapidly as possible to the neutralizing tank, which contains a solution of sodium sulfite. Sodium carbonate also may be used. Sulfur dioxide is boiled off and piped to the acidifiers. The resultant mixture of sodium benzenesulfonate and sodium sulfate is filtered at boiling temperature. The sodium sulfate precipitates out of the hot liquors and remains on the filter; the sodium benzenesulfonate mother liquor is pumped to a fusion pot.

The cast-iron fusion pot is charged with fused caustic soda and heated to 300°C by a gas or oil fire. At this temperature (300 to 320°C) the sodium benzenesulfonate is introduced under the surface of the caustic melt. About 3 moles of alkali per mole of sulfonate is employed. The temperature is maintained at 300 to 310°C for several hours and finally at about 380°C for 1 hr. After the fusion is completed (5 to 6 hr), the pot is emptied, and the melt is diluted with water or dilute phenol wash water from the previous charge. The sodium phenate–sodium hydroxide–sodium sulfate solution is acidified with sulfur dioxide obtained from the sulfonic-acid neutralization. A small amount of sulfuric acid is generally needed to complete the acidification. The crude phenol separates as the upper layer over an aqueous solution containing sodium sulfite and sodium sulfate. The phenolic layer is decanted and distilled under vacuum to yield refined phenol. The aqueous layer is treated with steam to remove residual phenol, and this distillate is used as make-up water. Part of the sulfite sludge is used for neutralizing the benzenesulfonic–sulfuric acid mixture, and the remainder may be recrystallized and dried to yield anhydrous sodium sulfite (by-product). Phenol of USP quality is obtained in about an 85 per cent by weight yield based on benzene.

In some plants the fusion melt is diluted with a minimum amount of water so that all the sodium sulfite does not go into solution. Undissolved sodium sulfite is separated by settling and centrifuging, and the clarified sodium phenate solution is sent to the acidifiers.

Chlorobenzene (Carbonate) Process



Reaction

$$C_6H_5Cl + Na_2CO_3 + H_2O \rightarrow C_6H_5OH + NaCl + NaHCO_3$$

90–95% yield

Material Requirements

Basis—1 ton phenol

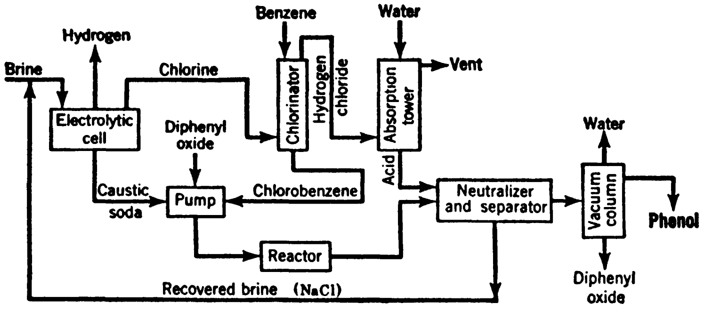
Chlorobenzene	2,500 lb
Sodium carbonate (anhydrous)	2,950 lb

Process

Chlorobenzene (1 mole), 10 per cent by weight of diphenyl oxide, and a 10 per cent aqueous sodium carbonate solution (1.25 moles) are introduced into a high-pressure pump. The diphenyl oxide is added to repress its formation during the hydrolysis reaction. The pump compresses the reactants to a pressure of about 3,000 psi, and the resulting emulsion passes through a mile-long copper tubular pressure system contained in an autoclave or furnace. There is enough turbulence in the tubes to maintain dispersion of the organic reactants. The reaction furnace is heated to a temperature of about 320°C, diphenyl oxide vapor under moderate pressure being used as the heating medium. The emulsion is pumped through the furnace system with recirculation and continuous discharge of a small portion, which is continuously made up by the entering charge. The reaction time is approximately 3 to 5 min.

The discharge passes through heat exchangers and coolers before the pressure is released. Two layers separate, a phenolic upper layer over an aqueous sodium bicarbonate solution. The upper layer is decanted and vacuum-distilled. Water and a small amount of unchanged chlorobenzene comes over as the forerun and is followed by the phenol. The diphenyl oxide is withdrawn from the bottom of the column for re-use. The sodium bicarbonate solution is treated with steam to remove residual phenol and is converted to sodium carbonate for re-use by the addition of caustic soda. Phenol of USP quality is produced in a 90 to 95 per cent yield by weight based on chlorobenzene.

Chlorobenzene (Caustic) Process



Reaction

$$C_6H_5Cl + 2NaOH \rightarrow C_6H_5ONa + NaCl + H_2O$$

$$C_6H_5ONa + HCl \rightarrow C_6H_5OH + NaCl$$

Side reaction:

$$C_6H_5ONa + C_6H_5Cl \rightarrow C_6H_5OC_6H_5 + NaCl$$

90–95% yield

Material Requirements

Basis—1 ton phenol

Chlorobenzene	2,500 lb
Caustic soda	2,740 lb

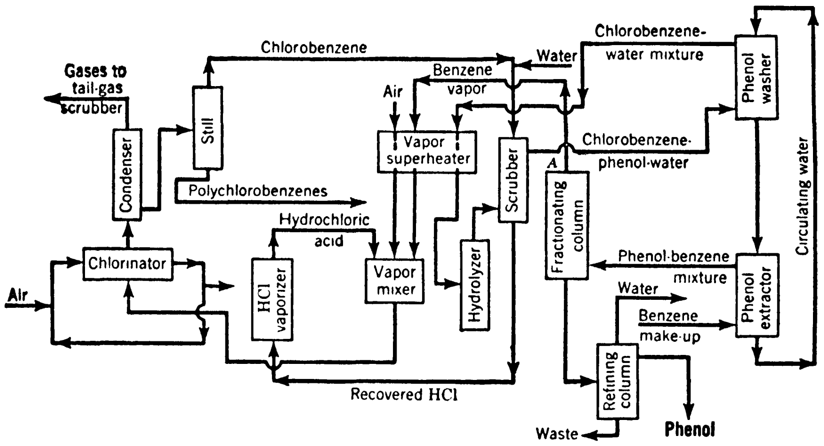
Process

A mixture of chlorobenzene, diphenyl oxide, and dilute caustic-soda solution in approximately the same ratios as shown for the afore-mentioned carbonate process is pumped through a steel-pipe heat exchanger to a reactor (contact furnace). Here hydrolysis takes place at about 5,000 psi and 360°C. By use of an efficient heat exchanger, the heat of reaction is sufficient to maintain the proper reaction temperature.

The reaction products, consisting of sodium phenate, sodium chloride, water, and unchanged reactants, are cooled by passing through the heat exchanger to the acidifier. Here the sodium phenate is converted to phenol by the use of hydrochloric acid. The phenol is decanted and distilled under vacuum to give phenol of USP quality. The yields are about the same as those in the carbonate process. The aqueous layer contains sodium chloride and some phenol which is removed by steam distillation.

The caustic process is particularly applicable when sodium chloride brine and benzene are used as raw materials. The brine is converted in an electrolytic cell to hydrogen, chlorine, and caustic soda. The benzene is chlorinated, yielding chlorobenzene and hydrochloric acid. The chlorobenzene is hydrolyzed, using aqueous caustic soda. The resulting sodium phenate is acidified by hydrochloric acid (by-product from chlorination), yielding phenol and brine. The latter is re-used in the beginning of the cycle. For details see *Chlorobenzene, Sodium Hydroxide* (*Caustic Soda*).

Regenerative (Raschig) Process



Reaction

$$C_6H_6 + HCl + \tfrac{1}{2}O_2\ (\text{air}) \xrightarrow[\text{Catalyst}]{\text{Cu}-\text{Fe}} C_6H_5Cl + H_2O$$

$$C_6H_5Cl + H_2O \xrightarrow[\text{Catalyst}]{SiO_2} C_6H_5OH + HCl$$

Combined:

$$C_6H_6 + \tfrac{1}{2}O_2 \longrightarrow C_6H_5OH$$

8–15% conversion per pass
72–85% yield

Material Requirements

Basis—1 ton phenol

Benzene	2,200 lb	Water	6,700 lb
Air	4,800 lb	Hydrochloric acid (20°Bé)	380 lb

Process

Benzene is converted to phenol in two catalytic vapor-phase stages. In the first stage, benzene is chlorinated with hydrochloric acid and air in the presence of a copper–iron (as chlorides) catalyst supported on a carrier at 200 to 230°C. The reaction is exothermic, necessitating external cooling; the conversion of benzene to chlorobenzene is about 10 per cent per pass.

In the second operation chlorobenzene is hydrolyzed in a contact furnace at about 500°C over materials containing catalytically active silicic acid. Approximately 10 per cent of the chlorobenzene is converted per pass to phenol and side-reaction products. These by-products are formed because of the presence of water and consist of diphenyl ether (oxydiphenyl) and tarry matter. However, only about 0.1 lb of total by-products are formed per lb of phenol produced, and these consist of polychlorobenzenes and the afore-mentioned products.

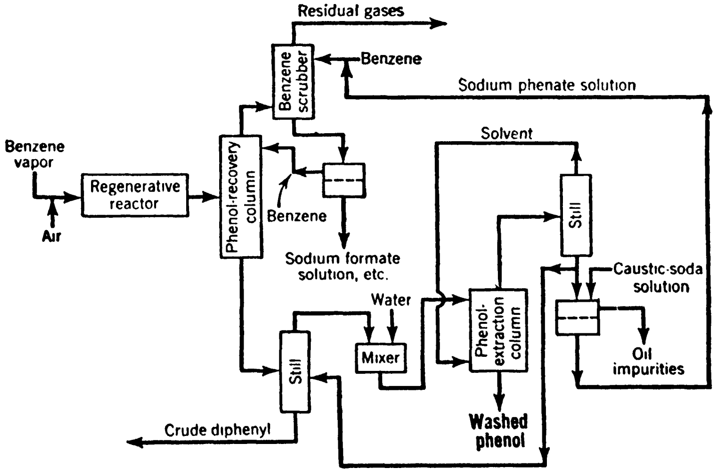
Referring to the flowsheet and starting at *A*, benzene vapor from the fractionating column is drawn at slight negative pressure through a tubular vapor superheater (500°C) and then to a vapor mixer. Here it is mixed with hydrochloric-acid vapors of 15 to 17 per cent strength coming from the vaporizer and with air, which previously was heated to about 500°C in the vapor superheater. The resultant vapor mixture passes into the chlorinator (contact furnace), which is maintained at 200 to 230°C by circulated cooling air. The chlorinated products (*ca.* 10 per cent conversion) and unchanged reactants pass to the condenser, where chlorobenzene is condensed and removed from the bottom. The vapors from the condenser are cooled further, yielding some benzene and scrubbed with hydrocarbon oil to absorb the remaining benzene before being released to the atmosphere. The benzene is used as make-up and is introduced back into the system at the bottom of the phenol extractor.

The chlorobenzene from the bottom of the condenser is distilled, yielding polychlorobenzene by-products and monochlorobenzene. Water is added to the latter, and the mixture is introduced into the top of the scrubbing column (scrubber). Here the reaction products from the hydrolyzer (contact chamber) are scrubbed, and the phenol is extracted. The excess water absorbs the hydrochloric acid from the vapors, and the recovered solution flows from the bottom of the scrubber to the hydrochloric-acid vaporizer, where it is subsequently vaporized. The vapors leaving the top of the scrubber consist of chlorobenzene, water, and the extracted phenol. They pass into the bottom of the phenol washer where hot water absorbs the phenol. The chlorobenzene–water vapors leave the top of the phenol washer and are heated to 400°C (by the hot products from the hydrolyzer in a heat exchanger) and finally to 500°C in a vapor superheater. The hot gases are blown through the hydrolyzer over a silica catalyst, which converts about 10 per cent of the chlorobenzene to phenol. The hydrolyzer reaction products are cooled to 200°C (by the incoming reactants in a heat exchanger) and then pass to the scrubber where the hydrochloric acid is recovered.

The phenol–water solution leaves the bottom of the phenol washer and passes through the phenol extractor where it is extracted by benzene. The water recirculates to the phenol washer. The phenol–benzene mixture leaves the top of the extractor and flows to the continuous fractionating column where the benzene is vaporized. The condensate, crude phenol (97 per cent), leaves the bottom of the fractionating column and is continuously distilled under vacuum to yield phenol of USP quality.

The efficiency of the hydrochloric-acid recovery system is about 97 per cent, which includes mechanical losses of hydrochloric acid, as well as losses in the form of polychlorinated benzenes. Although the conversion of chlorobenzene to phenol amounts to 8 to 15 per cent per pass, the over-all yield is 85 to 95 per cent. The over-all yield of benzene to phenol is 70 to 85 per cent by weight.

Benzene Oxidation Process



Reaction

$$C_6H_6 + \frac{1}{2}O_2 \rightarrow C_6H_5OH \qquad (80\%)$$

$$2C_6H_6 + \frac{1}{2}O_2 \rightarrow C_6H_5{-}C_6H_5 + H_2O \qquad (20\%)$$

8–10% conversion per pass
50–60% yield (phenol)

Material Requirements

Basis—1 ton phenol

Benzene	3,500 lb	Caustic soda	3.5 lb
Air	200,000 cu ft (STP)	Solvent (loss)	20 lb

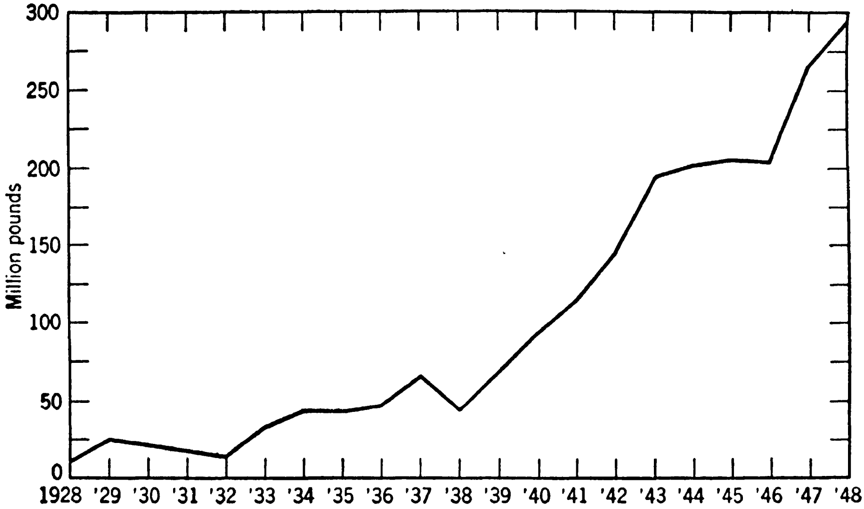
Process

Benzene vapor and air in equimolecular proportions are passed into a regenerative reactor at or slightly below atmospheric pressure. The reactor is so constructed that a reaction temperature of 600 to 800°C is attained. Because of the high temperature of reaction, the reactor is of the regenerative type in which entering gases are heated by the reaction products and vice versa. The reactor consists of a series of parallel passages, which are interconnected at intervals. It is built of firebrick and preferably with the reaction walls coated with boron oxide (to inhibit side reactions). The regenerators themselves are packed with firebrick. For best results the reactor should be so constructed and operated that the ratio of mass velocity of gases to hourly space velocity at 200°C is between 10 to 1 and 20 to 1: that is, mass velocity between 2,000 and 8,000 and hourly space velocity at 200°C between 200 and 400. The direction of flow of the gases is reversed every 60 sec. Less than 10 per cent of the benzene is oxidized per pass through the reactor. The nonbenzene components of the reacted gases consist of phenol, diphenyl, and fixed gases.

The gases leaving the reactor enter a phenol-recovery column (100 to 200°C) in which benzene is vaporized, scrubbed with cold benzene containing sodium phenate solution (equivalent to 4 per cent of phenol produced in the reactor), and recovered for re-use. Liquid benzene leaving the bottom of the benzene scrubber goes to a decanter, from which an aqueous layer of a solution of sodium salts of organic acids (chiefly sodium formate) is removed. The residual gases leaving the top of the benzene scrubber contain about 0.1 per cent benzene and sufficient combustible fixed gases (carbon monoxide, hydrogen, and methane) to be of some fuel value.

The phenol–diphenyl mixture (containing smaller amounts of other aromatic hydrocarbons) leaves the bottom of the phenol column and is charged to a product still, where it is distilled to yield crude phenol (2 to 20 per cent impurities) as overhead and a residue rich in diphenyl. The phenolic overhead from the column is condensed, mixed with one-fourth its weight of water, and fed to an extraction column, where it is passed countercurrent to solvent naphtha (or other aliphatic hydrocarbon solvent). The weight ratio of solvent to phenol in the extraction is of the order of 1 to 3 parts of solvent per unit weight of phenol. The washed phenol leaving the bottom of the column is of approximately 98 per cent purity.

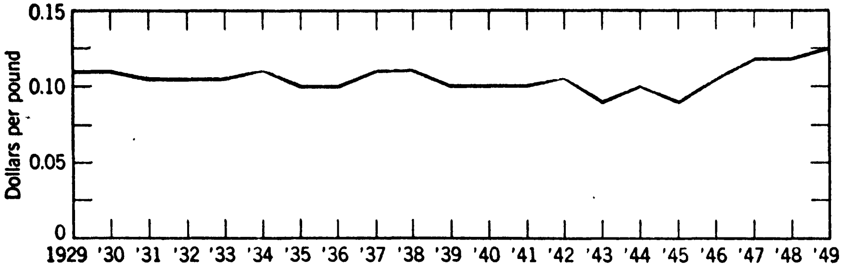
The hydrocarbon solvent containing impurities removed from the phenolic feed leaves the top of the column and goes to a still for solvent recovery. The impurities leaving the bottom of the still column contain some phenol, and so this fraction is treated with caustic-soda solution and allowed to separate into two phases. The aqueous layer, containing sodium phenate, is sent back to the benzene scrubber. The oil layer is discarded.



Production—Phenol

Use Pattern

	1947 (est.), per cent
Phenolic resins	60
Chemical manufacture	20
Petroleum refining	6
Disinfectant and insecticides	5
Miscellaneous and export	9
	100



Price—Phenol

Miscellaneous

Properties. White, crystalline mass, which turns pink or red from impurities or on exposure to air and light. Absorbs water from the air and liquefies. Has a sharp burning taste and distinctive odor. It is a strong, corrosive poison.

Mol. wt.	94.11	M.P.	42-43°C
Sp. gr.	1.071 25°C/4	B.P.	181.4°C

Soluble in alcohol, ether, chloroform, glycerine, carbon disulfide, and water (8.2 g per 100 g at 15°C, in all proportions above 65.3°C).

Flash point (closed cup)	175°F
Ignition temperature	1,319°F
Vapor density (air = 1)	3.24

Grades. Solid: USP (98 per cent minimum), C.P., and synthetic. Liquid: commercial (90 to 92 per cent and 82 to 84 per cent containing some cresols and water), and crude.

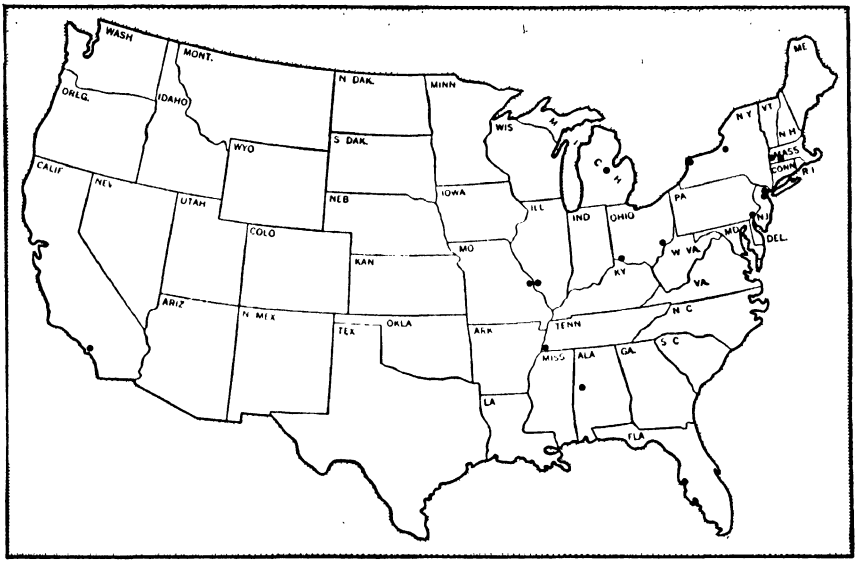
Containers and Regulations. Tank cars, galvanized drums, drums, cans, and bottles. Should be stored in tightly closed containers to prevent water absorption and in the absence of light, which causes discoloration. Class B "Poison" ICC shipping label required.

Economic Aspects

At the end of World War I, stocks of phenol held in the United States were estimated as sufficient to supply all demands for six years; yet the supply was exhausted within three years primarily in the manufacture of phenol–formaldehyde resins. Since that time, production and demand have continued to rise, and no sharp decrease in consumption may be predicted for the future. In fact, the accelerated manufacture of just one item, weed-control chemicals, may shortly require 40,000,000 to 100,000,000 lb phenol annually, in contrast to the current 20,000,000 lb requirement.

Prior to World War I, nearly all the phenol manufactured in the United States was natural phenol derived from coke-oven operations and coal-tar distillation. In 1947 less than 7 per cent of the phenol produced was natural phenol; the remainder was synthetic.

The first synthetic process was the batch sulfonation and alkali-fusion process, which used benzene as the raw material. The chlorobenzene liquid-phase hydrolysis process (carbonate process) appeared in 1925 and gradually replaced the older sulfonation process, largely because of manufacturing economy. The only sulfonation processes remaining today in large plants are modified streamlined processes operated by producers whose plants were largely paid for by earlier operations and who also manufacture the raw materials themselves. On the other hand, about 40 per cent of total United States production of synthetic phenol was derived from sulfonation processes in 1947.



Location of Synthetic-Phenol Plants

In recent years the regenerative process, the benzene-oxidation process, and the chlorobenzene (caustic) process have appeared and are believed to be competitive with the original liquid-phase chlorobenzene hydrolysis process. Undoubtedly the remains of the sulfonation process will gradually disappear.

Synthetic-phenol plants vary greatly in size; the usual range is 10,000,000 to 100,000,000 lb per yr, with the majority in the range of 10,000,000 to 20,000,000 lb. Investment costs for complete plants of this size will vary from 7 cents to 17 cents per annual pound phenol capacity, depending on the process used. In general, the sulfonation process requires the least investment, and the regenerative process the greatest.

Proponents of the regenerative process claim only 0.1 lb by-products (polychlorobenzene, diphenyl compounds, and tarry matter) per lb phenol produced, against 2 to 5 lb in the sulfonation, chlorobenzene–liquid-phase hydrolysis, and oxidation processes. A further claimed advantage of the regenerative process is absence of cresols in the product derived from toluene contamination of the benzene used.

Natural phenol is recovered largely from the tar-acid fraction obtained in the distillation of coal tar (see *Cresol*). Yields vary from 0.3 to 0.7 per cent of the coal tar processed. At times phenol has been recovered from petroleum cresylic-acid fractions (see *Cresol*).

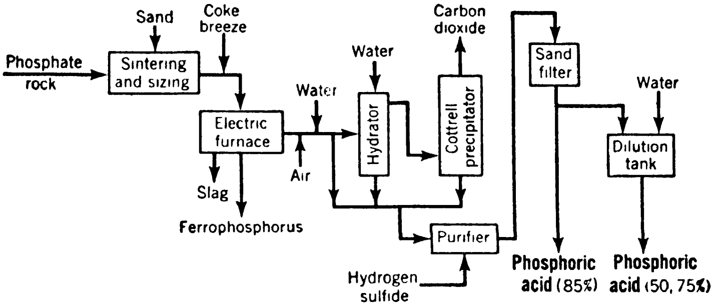
Recently a new process has been proposed, which involves the oxidation of isopropyl benzene to produce acetone and phenol simultaneously in a single operation. The raw material is manufactured by alkylating benzene with propylene.

PHOSPHORIC ACID

(ORTHOPHOSPHORIC ACID)

H_3PO_4

From Phosphate Rock by Electric Furnace



Reaction

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 2P + 5CO + 3CaSiO_3$$

$$2P + 5CO + 5O_2 \rightarrow P_2O_5 + 5CO_2$$

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

87–92% yield

Material Requirements

Basis—1 ton phosphoric acid (100%)
(plus 4,600 lb slag)

Phosphate rock (70 BPL)	4,900 lb	Carbon electrode consumption	17 lb
Sand (silica)	1,495 lb	Air (minimum)	100,000 cu ft
Coke breeze	880 lb	Electricity	4,070 kw-hr

Process

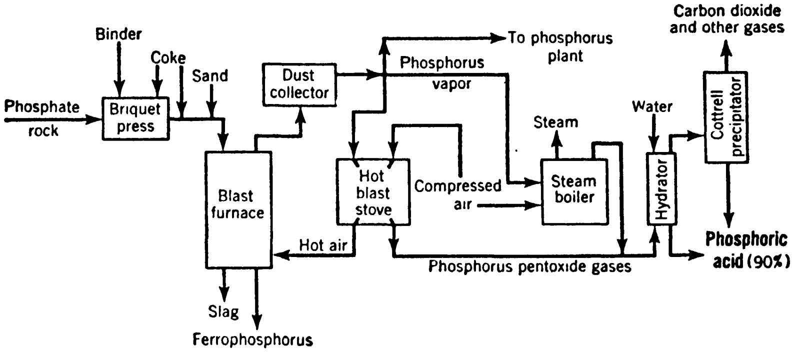
In the electric-arc-furnace process, phosphate rock is reduced to elemental phosphorus by the action of coke and heat in the presence of sand. Subsequent oxidation by air to phosphorus pentoxide followed by hydration yields phosphoric acid.

Phosphate rock is charged into a sintering oven, where it is nodulized to facilitate escape of phosphorus vapors in the electric furnace and to prevent the entrainment of dust or fines (in the vapors). The raw material is sized, and the fines are returned to the sintering oven. Coke (generally in the form of breeze) and sand are added in carefully controlled ratios, determined by rock analysis, to the sintered rock, and the mixture is charged into the shaft of an electric furnace. In the shaft hang three carbon electrodes, which are connected to a three-phase alternating current. The charge, on reaching the level of the arc, is fused at approximately 2,400°F, resulting in the reduction of the phosphate rock with liberation of elemental phosphorus vapors. Since phosphate rock usually contains fluorides as impurities, calcium fluoride and fluosilicates are also formed. The slag (mostly calcium silicate) from the furnace is usually tapped periodically and subsequently crushed for use as aggregate for road construction. Ferrophosphorus (resulting from the iron impurities) runs out with the slag. The amount of this material produced may be increased by adding iron slugs to the furnace charge. The ferrophosphorus is separated from the slag and marketed.

The gases from the furnace, phosphorus and carbon monoxide, are withdrawn from the furnace by means of a fan. In the one-step system, a current of air is drawn down through the charge by the suction induced by the fan. The two-step method produces phosphorus, which is stored for subsequent processing (see *Phosphorus*). The two currents (reaction gases and air) mix in the flue at a temperature sufficient to burn the phosphorus to phosphorus pentoxide (P_2O_5) and the carbon monoxide to the dioxide. The gases pass into a tall packed tower, where they are sprayed with water (forming a mist of phosphoric acid), and thence through a Cottrell electrostatic precipitator made of graphite (to resist the action of hydrofluoric acid) to remove any remaining phosphoric acid.

The crude phosphoric acid (85 per cent) is generally purified with respect to arsenic by the action of hydrogen sulfide. Depending on conditions, the acid may be purified further by adding sulfuric acid to remove calcium salts. Sufficient sulfuric acid is used to precipitate calcium sulfate and also to leave a slight excess to inhibit the corrosive action of the phosphoric acid. This slight excess of sulfuric acid permits the use of lead-lined equipment. Residual hydrofluoric acid may be removed by the addition of finely powdered silica. These purification steps usually take place before arsenic removal. The excess silica, calcium sulfate, arsenic trisulfide, and any suspended material are removed by passage of the acid through a sand filter. The clarified phosphoric acid (85 per cent) may be diluted with water to yield 75 per cent and 50 per cent acid. An over-all yield of about 90 per cent is realized on the calcium phosphate content of the rock raw material.

From Phosphate Rock by Blast Furnace



Reaction

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 2P + 5CO + 3CaSiO_3$$

$$2P + 5CO + 5O_2 \rightarrow P_2O_5 + 5CO_2$$

$$P_2O_5 + 3H_2O \rightarrow 2H_3PO_4$$

85–90% yield

Material Requirements

Basis—1 ton phosphoric acid (100% H_3PO_4)
(equivalent to 72% P_2O_5)

Phosphate rock ($27\%\ P_2O_5$)	5,050 lb	Coke	7,000 lb
Sand (silica)	1,500 lb	Briquet binder	500 lb
		Air	450,000 cu ft

Process

The raw materials and reactions in the blast-furnace process are essentially the same as those of the electric-furnace process. The shaft furnace used is similar in appearance to the blast furnaces used by the steel industry.

Phosphate rock is pulverized and mixed with ground coke, which serves as the reducing agent. A binder is added, and the mixture is compressed at about 5,000 psi into briquets, which are dried (to a moisture content of less than 1 per cent) in a continuous dryer. The briquets, sand (as flux), and additional coke are charged into the top of the shaft of the blast furnace. Preheated air (from the hot blast stoves) is blown in at the bosh (the lower part of the furnace). The blast develops a temperature of 2,400 to 2,500°F, which furnishes the necessary reaction heat. Slag (consisting chiefly of calcium silicate) is tapped from the furnace hearth once an hour, and the heavier ferrophosphorus (formed from the iron impurities in the rock and coke) is tapped every 12 hr.

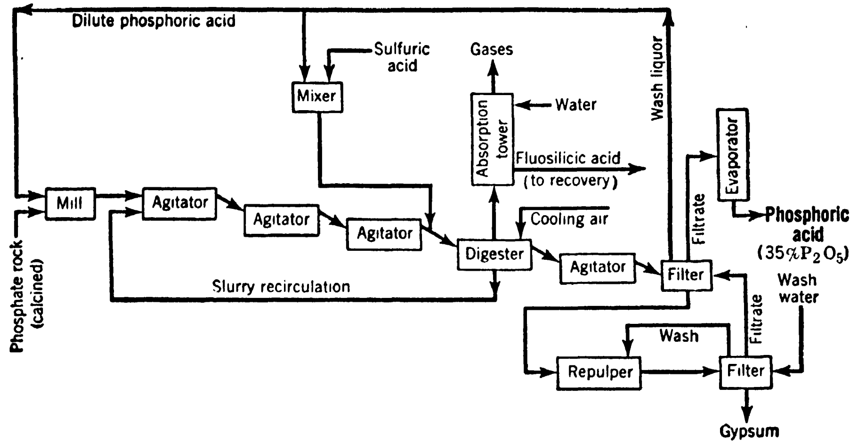
The gas, containing phosphorus, carbon monoxide, and nitrogen, passes from the top of the shaft through cyclone dust collectors and special fume collectors. The clean gas may be split into two or three portions. One portion may be passed through phosphorus condensers to produce the elemental product and anhydrous phosphorus pentoxide. See *Phosphorus* for details. A second portion may be passed into special boilers for steam generation. The phosphorus pentoxide formed in the steam boiler is added to the main gas stream.

The third portion (generally the largest) is passed into hot blast regenerative stoves, where it is oxidized to phosphorus pentoxide. The stoves furnish the preheated air for the furnace blast. The gaseous products from the stoves and steam boilers are led into hydrating towers for hydration and cooling and thence through Cottrell precipitators for entrained phosphoric-acid removal. The condensed acid (85 to 95 per cent H_3PO_4) may be purified (arsenic removed) by treatment with hydrogen sulfide and subsequent filtration. About 95 per cent of the phosphorus in the rock raw material is volatilized, giving a yield of about 90 per cent based on the phosphorus pentoxide content of the raw material and product.

Two-Step Process. A considerable amount of phosphoric acid is obtained from phosphorus (produced by thermal methods) using the two-step process. In the first step, phosphate rock is reduced to elemental phosphorus, condensed, and stored (see *Phosphorus*). In the second step, the phosphorus is pumped as a liquid through a spray burner into an acid-proof brick-lined tower. The air for the oxidation is introduced in both the spray nozzle and the top of the tower. The oxidized phosphorus vapor (P_2O_5) passes down the tower where it is hydrated (in the lower part) by a fine spray of water. The phosphoric-acid mist is recovered by scrubbing in packed towers.

The acid produced by the two-step method is very pure and requires no elaborate purification system. This method does not burn the by-product carbon monoxide to the dioxide, thus affording a means of recovering this material (see *Phosphorus*). Phosphoric acid of strength as high as 116 per cent (84 per cent P_2O_5) may be prepared from phosphorus. This acid bears the same relation to regular phosphoric acid as oleum does to sulfuric acid.

From Phosphate Rock by Dorr Strong-Acid Process



Reaction

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 2H_3PO_4 + 3(CaSO_4 \cdot 2H_2O)$$

92–93% yield

Material Requirements

Basis—1 ton phosphoric acid (100%)

Phosphate rock (70 BPL)	4,880 lb
Sulfuric acid (94%)	4,040 lb

Process

The sulfuric-acid or wet process produces phosphoric acid by the action of sulfuric acid on phosphate rock accompanied by the precipitation of calcium sulfate.

Phosphate rock is charged into a special ball mill, where it is ground in a dilute solution of phosphoric acid obtained as a filtrate from an ensuing operation. The slurry passes through a series of Dorr agitators, where reaction with sulfuric acid takes place. Separation of the resulting acid from the calcium sulfate precipitate, as well as washing of the precipitate, is carried out in a continuous-countercurrent decantation system.

The reaction system consists essentially of five agitators in series. Concentrated sulfuric acid (94 per cent), diluted with weak phosphoric acid, is introduced between the third and fourth agitators. The reaction takes place chiefly in the fourth agitator (the digester). The heat of reaction is considerable and is removed by blowing cooling air through the solution. As a result an appreciable amount of water is evaporated.

The air, water vapor, and gaseous impurities are carried off into an absorber where fluosilicic acid (H_2SiF_6) is recovered by spraying the gases with water. A considerable portion of the reaction mixture is recycled from the fourth agitator (digester) back to the first agitator. The rate of recycle is adjusted to maintain correct sulfuric-acid concentration and reaction time. The proper reaction time promotes formation of large crystals of calcium sulfate (gypsum) and facilitates subsequent filtration and washing operations. The temperature in the digester is maintained low enough to insure precipitation of gypsum ($CaSO_4 \cdot 2H_2O$) rather than anhydrite ($CaSO_4$), which would subsequently hydrate and cause pipe plugging.

The slurry from the digester passes through the fifth agitator to a continuous rotary filter. The filtrate is finished phosphoric acid (about 45 per cent), which may be further concentrated by evaporation. Wash liquor from the filter is a dilute solution of phosphoric acid, which is used to dilute the sulfuric acid and to charge the ball mill.

The filter cake, after washing, is charged into a tank where it is repulped with wash liquor from a second filter in which the repulped slurry is filtered. Filtrate from this filter serves as the wash liquor for the first one. The second filter cake is washed with fresh hot water. The washed filter cake, gypsum, is discharged to waste.

The filtrate from the first filter (phosphoric acid) is charged into lead-lined evaporators containing lead steam coils. The acid is generally concentrated to 35°Bé, at which gravity it contains about 35 per cent P_2O_5 (approximately 50 per cent H_3PO_4). It may be concentrated to 70 per cent acid or to a specific gravity of 50°Bé (50 per cent P_2O_5). The evaporator must be operated below 150°C, because above this temperature orthophosphoric acid (H_3PO_4) is slowly converted into pyrophosphoric acid ($H_4P_2O_7$). By means of the process described, about 95 per cent of the phosphorus pentoxide content of the rock is dissolved, and, of this, 97 to 98 per cent is recovered as product.

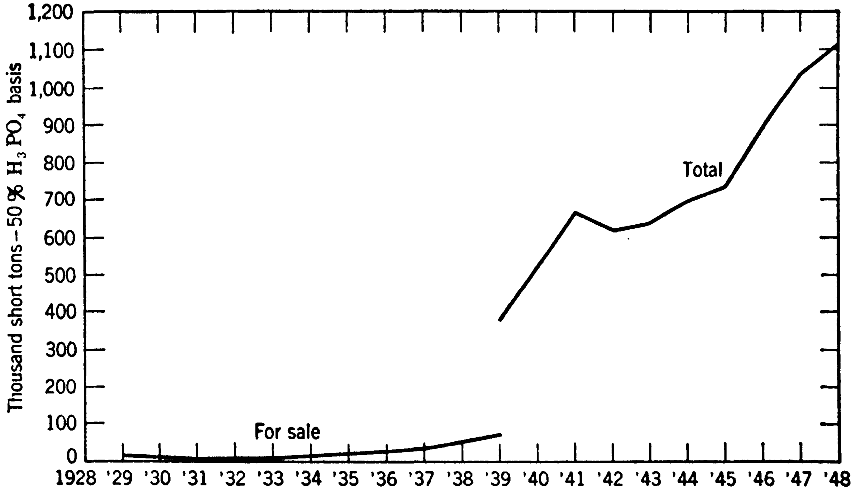
Other Phosphorus-Containing Acids. Phosphoric acid (H_3PO_4) may be converted into pyrophosphoric acid ($H_4P_2O_7$) and metaphosphoric acid (HPO_3) by heating. Pyrophosphoric acid is formed at 250 to 260°C. On heating either the ortho- or pyro- to a red heat, metaphosphoric acid is formed. The latter may also be prepared by treating phosphorus pentoxide with the calculated amount of cold water.

Raw Material

Phosphate rock, also known as rock phosphate, phosphorite, and raw phosphate, is the primary source of practically all phosphatic chemicals. The rock is obtained chiefly from deposits in Florida, Tennessee, and the Western States. These deposits are classified roughly as residual, replacement, and sedimentary. Residual phosphate (for example Tennessee brown rock) is derived from phosphatic limestone. Replacement phosphate (for example Florida soft rock) is phosphatized limestone formed by the reaction of limestone and phosphoric acid of organic origin. The sedimentary phosphates, believed derived from marine organisms, are the principal deposits of which Florida land pebble, Florida hard rock (boulder phosphate) and river pebble are the chief varieties. The sedimentary deposits occur in irregular pockets of many sizes embedded in clay or sand. Western phosphates, usually found in fissure veins between walls of limestone and clay or shale, are mined by underground methods. The Florida and Tennessee phosphates are found usually in surface deposits and are worked by open-cut mining methods.

Virtually all commercial deposits of phosphate rock are amorphous, impure varieties of the mineral, fluorapatite ($Ca_{10}(PO_4)_6F_2$). The workable deposits contain from 18 to 90 per cent available tricalcium phosphate, $Ca_3(PO_4)_2$, known to the trader as BPL (bone phosphate of lime), and are evaluated on this basis. The deposits generally average above 60 per cent BPL, and approximately three fourths of the phosphate rock marketed contains between 70 and 76 per cent BPL. Inferior rock is processed by beneficiation procedures to raise the BPL content of the rock.

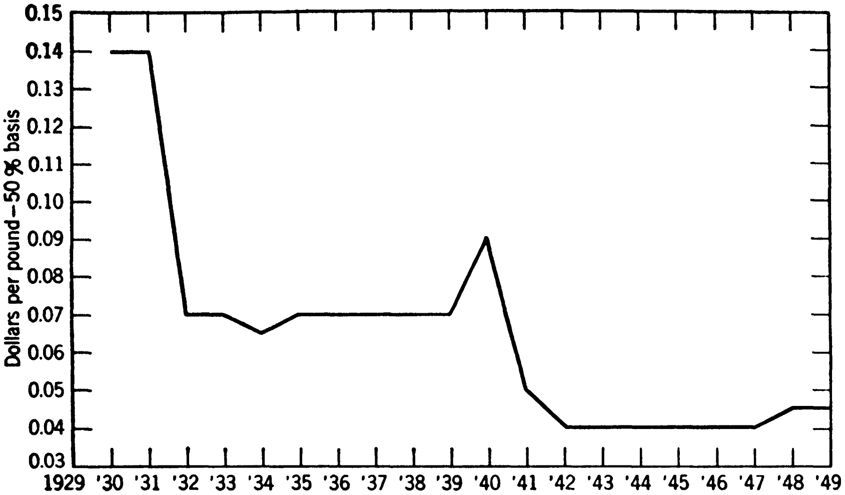
The chief impurities in domestic phosphate rock are iron, aluminum, and silicon oxides, as well as calcite, magnesite, dolomite, sand, clay, and organic matter. Most of the undesirable impurities are removed in the washing and sintering operations prior to phosphoric-acid manufacture.



Production—Phosphoric Acid

Use Pattern

Phosphates (sodium, ammonium, calcium) Superphosphate Metal treatment (rustproofing) Soft drinks and flavoring sirups Pharmaceuticals Other (including sugar refining, gelatin manufacture, pickling of steel, and water treatment)	No breakdown available



Price—Phosphoric Acid

Miscellaneous

Properties. Colorless, crystalline solid.

Mol. wt.	98.00	M.P.	42.35°C
Sp. gr.	1.834 (18.2°C)	B.P.	Loses ½H_2O at 213°C

Soluble in water (2,340 g per 100 ml at 26°C), and alcohol.

Commercial phosphoric acid is a clear, colorless, sparkling, mobile liquid which reaches sirupy consistency at higher concentrations (85 per cent). At 88 per cent concentration, a crystalline hydrate, $H_3PO_4 \cdot \frac{1}{2}H_2O$, separates at room temperature.

Grades. Technical (50, 75, and 85 per cent), food (50 and 75 per cent), USP (10 and 85 per cent), 90 per cent acid, 100 per cent acid (75 per cent P_2O_5), and commercial (47 and 54 per cent P_2O_5).

Containers and Regulations. Rubber-lined tank cars, tank trucks, drums, barrels, glass carboys, casks, and bottles. White ICC shipping label required.

Economic Aspects

Phosphoric acid is one of the products of a comparatively new phosphorus technology, which, although inorganic in nature, is believed by many to offer potentialities similar to the technology of carbon compounds (organic-chemical technology). Although the future may lie in this direction, phosphoric acid has been made for many years by the wet process for a limited number of uses. The advent of the commercial electric-furnace process (1920) was responsible for purer, cheaper acid and the recent strides in production.

Competition between the two processes centers around cost, concentration, and purity of the product. The wet process cannot economically yield much greater than 50°Bé (50 per cent P_2O_5) acid, but, since it is cheap and impurities make little difference, it is almost all used in the manufacture of fertilizer (triple superphosphate) and various purified salts. The product of the electric-furnace process is concentrated and pure and is used therefore in the food and high-grade chemical fields. At present more than 50 per cent of total acid production is from phosphorus, whereas the figure was reversed in 1941, the first year complete data were compiled.

Wet-process plants in the range of 100 to 125 tons phosphoric acid (calculated as 100 per cent H_3PO_4) per day cost about $40 per annual ton capacity, exclusive of crushing and grinding equipment. The plant investment for the electric-furnace process is twice that for the wet process, but this is overshadowed somewhat by the ability of the former to use low-grade phosphate rock as a raw material. Recent advances in phosphate-rock beneficiation should benefit both processes by making larger quantities of domestic rock available. This advance, of course, is actually of much greater value to the larger superphosphate industry.

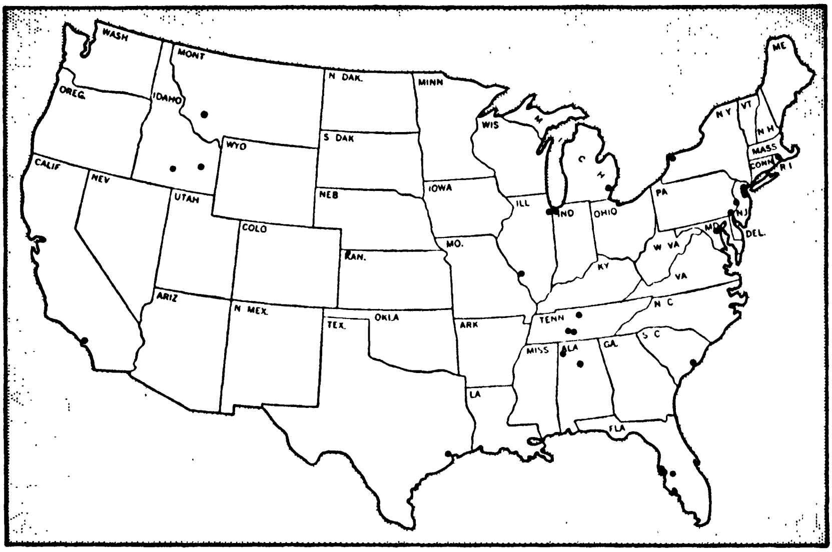
Both processes are plagued with by-products of low value which require disposal. Calcium sulfate waste from the wet process is not utilized at present, and the slag, carbon dioxide, and ferrophosphorus from the electric furnace have only limited uses.

The last blast-furnace plant in the United States shut down in 1939 and has not yet resumed operations. This furnace had a daily capacity of 125 tons of phosphorus pentoxide per day.

Although it is only a minor acid, manufacture of phosphoric acid is a large-scale operation. Many wet-process plants have capacities in the range of 60 to 180 tons of acid (calculated as 100 per cent) per day.

Of the two processes commonly used in the electric-furnace method, the one-step process appears to be most economical when the plant is located near both the raw-material source and the market for the acid. In many cases the two-step process, in which elemental phosphorus is condensed and subsequently converted to the acid, is used, inasmuch as the phosphorus may be shipped to a location near the acid market for conversion. In this case the furnace is located near the phosphate-rock deposits.

The future of the phosphoric-acid industry appears bright with an expanding phosphorus chemical industry in prospect and the entry of the acid into fields formerly dominated by sulfuric acid, such as concentrated fertilizers.



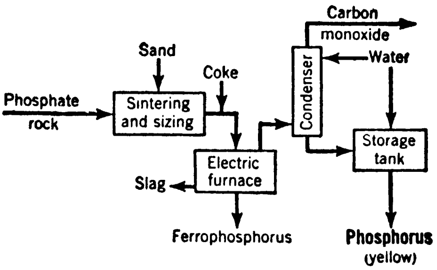
Location of Phosphoric-Acid Plants

PHOSPHORUS

(YELLOW PHOSPHORUS)

P_4

From Phosphate Rock (Electric Furnace)



Reaction

$$2Ca_3(PO_4)_2 + 10C + 6SiO_2 \rightarrow P_4 + 6CaSiO_3 + 10CO$$

92–95% yield

Material Requirements

Basis—1 ton phosphorus (yellow)

Calcium phosphate (70 BPL)	15,000 lb	Coke	2,650 lb
Sand (silica)	4,450 lb	Carbon electrode consumption	50 lb

Process

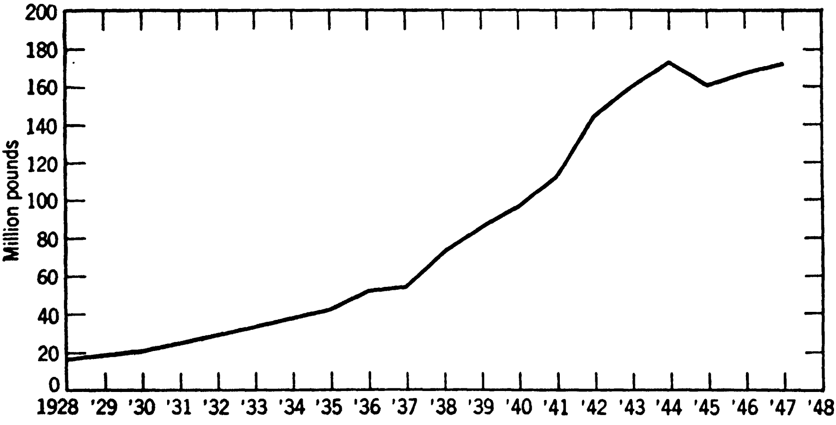
Yellow phosphorus (also known as white phosphorus) is produced by reducing phosphate rock (calcium phosphate) with carbon (coke) in the presence of silica (sand); the necessary heat of reaction is furnished by an electric-arc or blast furnace.

Since phosphorus is the intermediate product in the two thermal processes for phosphoric-acid manufacture, a detailed description of both the electric-arc and fuel-fired blast furnace is given in the chapter on phosphoric acid. A description of the more important of the two processes, the electric-arc furnace, is repeated here briefly.

Sintered phosphate rock, coke, and sand (as flux) are charged into the shaft of an electric-arc furnace. On reaching the level of the arc, the charge is fused at a temperature of 1,300 to 1,500°C, resulting in the liberation of elemental phosphorus vapors and carbon monoxide gas. Calcium silicate slag and ferrophosphorus are tapped periodically from the base of the furnace. The top of the furnace shaft is enclosed to exclude air, which would result in the oxidation of the elemental phosphorus.

The furnace gases pass into coolers, where the vapors are liquefied and separated from the carbon monoxide gas. The latter is vented to be used as fuel, or it may be recovered for other uses by any suitable means. The condensed phosphorus is collected and stored under water as a liquid. When molten phosphorus is cooled, the temperature can be reduced much below the melting point (*ca.* 44°C) without solidification, owing to the effects of undercooling. Storage tanks are usually fitted with steam coils, although the liquid material under water is shipped in regular tank cars. Phosphorus may be solidified into cakes and sticks and is shipped under a protective covering of water in these forms in tins and barrels. The yield of phosphorus based on the calcium phosphate content of the rock raw material is 92 to 95 per cent.

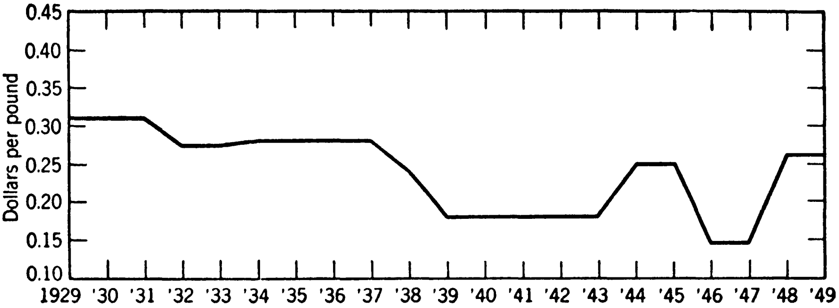
Most of the yellow phosphorus produced is ultimately utilized in the production of phosphoric acid and phosphates. However, when it is used directly in the match and allied industries, the element is usually converted first to less poisonous red phosphorus. This allotropic form may be produced by heating yellow phosphorus to approximately 240°C in the absence of air or in an inert atmosphere.



Production—Phosphorus

Use Pattern

	1947 (est.), per cent
Phosphoric acid and inorganic phosphates	75
Organic phosphorus compounds	15
Matches	3
Miscellaneous	7
	100



Price—Phosphorus (Yellow)

Miscellaneous

Properties. White or pale yellow, waxlike, translucent crystallizable solid with a distinctive, disagreeable odor. It is luminous and phosphorescent in the dark and is exceedingly poisonous.

Mol. wt.	123.92	M.P.	44.1°C
Sp. gr.		B.P.	280°C
Solid	1.82 (20°C)		
Liquid	1.745 (44.5°C)		

Flash point	Spontaneously ignites in air
Ignition temperature	300°C

Soluble in alcohol (0.4 per cent), carbon disulfide (1,000 g per 100 g at 10°C), benzene (1.5 g per 100 g at 0°C, 10 g per 100 g at 81°C), chloroform, and ammonia. Insoluble in water (0.0003 per cent cold).

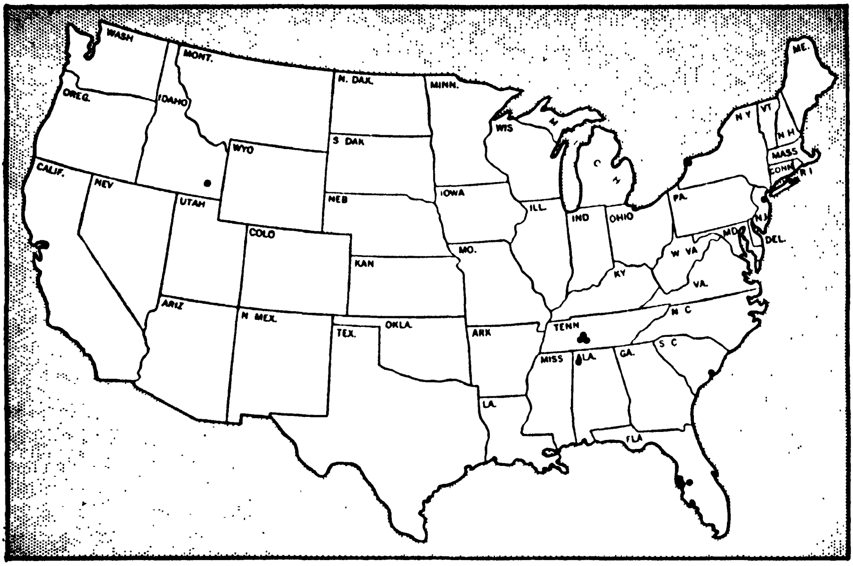
Grades. Technical, and USP (liquid, cakes, and sticks).

Containers and Regulations. Tank cars, steel barrels, and tins. Ignites spontaneously in air and, therefore, is packed, stored, and handled under water. Yellow ICC shipping label required.

Economic Aspects

A number of the general factors previously discussed (see *Phosphoric Acid*) apply also to phosphorus. The same general type of electric furnace is used for phosphorus production as for phosphoric acid, except that modifications must be made to eliminate air from the hot vapors leaving the furnace in order to avoid oxidation. Accordingly, the by-product gas in this case is carbon monoxide instead of carbon dioxide.

In many cases where phosphoric acid is the desired end product, phosphorus is condensed and recovered at the electric-furnace plant and shipped to the point of consumption to be converted to phosphoric acid. In a theoretical economic sense, this is a wise procedure, since air and water necessary for the conversion need not be shipped. The vagaries of freight-rate structure often change this situation and make the alternate procedure the cheaper.



Location of Phosphorus Plants

Aside from phosphoric acid and its principal derivative, triple superphosphate, phosphorus is the raw material for many products whose uses are increasing yearly. The entrance of phosphorus into an entirely new chemical field in which phosphorus may be the basic element, as carbon is in the organic-chemical field, has just begun and leads to interesting speculation. In this connection, consideration should be given to new compounds containing phytin phosphorus, which are now appearing on the market. These phytin compounds are not derived from phosphorus but are an indication of the type of phosphorus-containing compounds that may be expected in the future.

The early phosphorus furnaces were quite small and of a batch nature. Improved technology has led to larger continuous furnaces, and many now have capacities of 10 to 25 tons of phosphorus per day. Some plants find it economical to operate only one furnace, whereas others may have three to five furnaces, either of the new larger type or as small as 3 tons per day capacity each. Furnace costs may vary from $100 to $150 per annual ton capacity, depending on furnace size. The complete plant will cost 2 to 2½ times as much.

Careful chemical control is a necessity in furnace operation, since slight changes in the ratio of the various raw materials or in their composition may lead to yield losses.

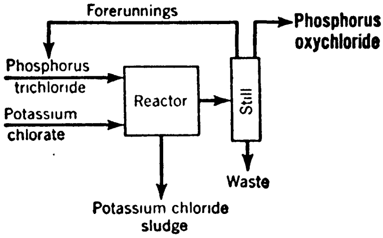
The primary product of the phosphorus furnace is yellow phosphorus, which is highly unstable to oxidation. In certain cases it is converted to the more stable red phosphorus by the action of heat. The latter must be used in the match industry because of prohibitive taxes on matches containing yellow phosphorus.

PHOSPHORUS OXYCHLORIDE

(PHOSPHORYL CHLORIDE)

$POCl_3$

From Phosphorus Trichloride and Chlorates



Reaction

$$3PCl_3 + KClO_3 \rightarrow 3POCl_3 + KCl$$

90–95% yield

Material Requirements

Basis—1 ton phosphorus oxychloride

Phosphorus trichloride	1,890 lb
Potassium chlorate	570 lb

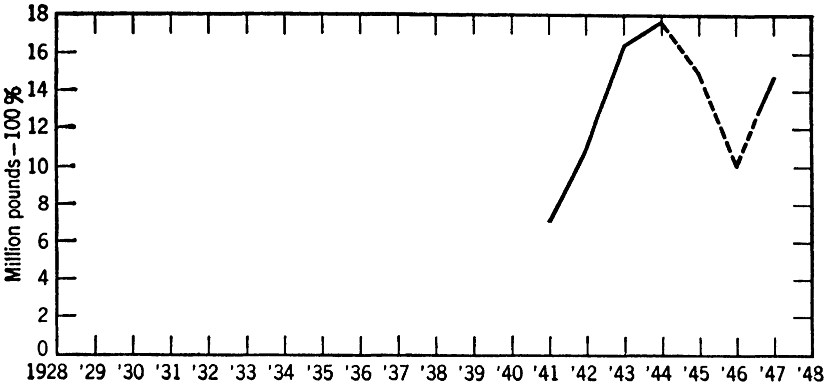
Process

Phosphorus oxychloride is produced by oxidizing phosphorus trichloride with potassium or sodium chlorate. The phosphorus trichloride is obtained by chlorinating yellow phosphorus in an inert atmosphere (carbon dioxide) and distilling the crude product.

Phosphorus trichloride is charged into an iron or nickel reaction kettle connected with a reflux condenser. Dry, powdered potassium chlorate is gradually added to the liquid in a weight ratio of about 1 part of chlorate to 3 parts of phosphorus trichloride. The chlorate is added in small portions so that only gentle ebullition takes place.

An alternate procedure is to charge pulverized potassium chlorate (16 parts) to the kettle. To avoid the risk of explosions, the chlorate is covered with a layer of phosphorus oxychloride (20 parts). Phosphorus trichloride (50 parts) is gradually added to the mixture until the reaction is completed.

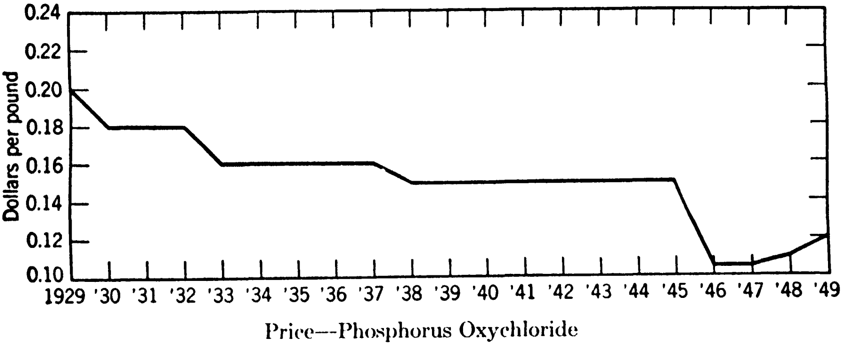
After the last reactant has been added, the mixture is fractionally distilled; any unreacted phosphorus trichloride is contained in the fore-runnings. The main fraction, distilling between 105 and 107°C, contains the colorless product. The yield of phosphorus oxychloride is about 95 per cent. The liquid product is stored and packaged in moisture- and acid-proof containers since phosphorus oxychloride slowly hydrolyzes into phosphoric and hydrochloric acids.



Production—Phosphorus Oxychloride

Use Pattern

	1947 (est.), per cent
Phosphate plasticizers	70
Sulfa drugs	20
Other	10
	100



Price—Phosphorus Oxychloride

Miscellaneous

Properties. Clear, colorless, fuming liquid.

Mol. wt.	153.35	M.P.	2.0°C
Sp. gr.	1.675 (15°C)	B.P.	107.2°C

Decomposes in water and alcohol.

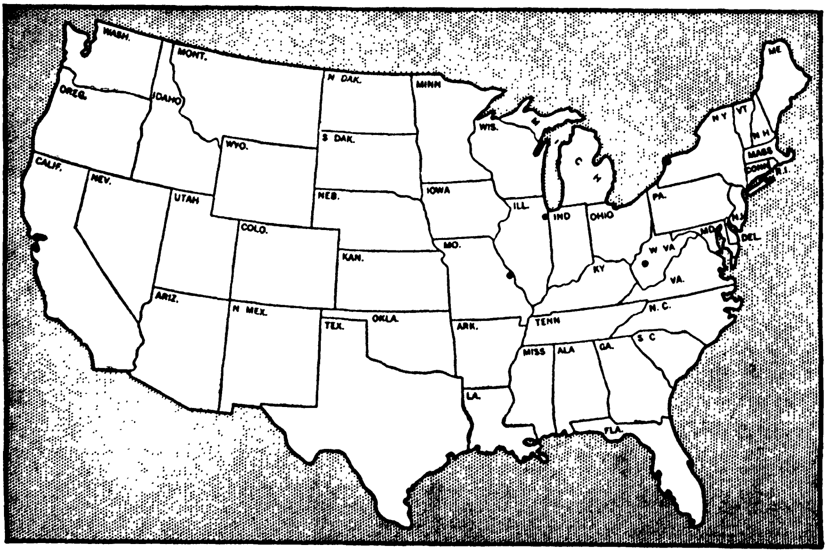
Grades. Technical (99.5 per cent).

Containers and Regulations. Nickel-lined tank cars and drums, and steel-jacketed lead carboys. White ICC shipping label required.

Economic Aspects

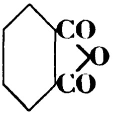
Phosphorus oxychloride is one of the phosphorus-containing intermediates that may become of much greater importance in an expanded phosphorus technology. The entire output is presently used in organic synthesis, chiefly in the manufacture of phosphate esters.

The manufacturing operation is batchwise and requires only simple plant equipment. The operation is hazardous, however, as is any process in which chlorates are handled. In the past, a process using sulfuryl chloride (SO_2Cl_2) as one of the reactants has been used, but current production uses only potassium chlorate. The reaction for the older process was: $PCl_3 + SO_2Cl_2 \rightarrow POCl_3 + SOCl_2$.

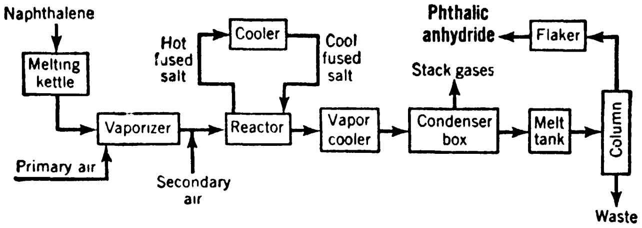


Location of Phosphorus Oxychloride Plants

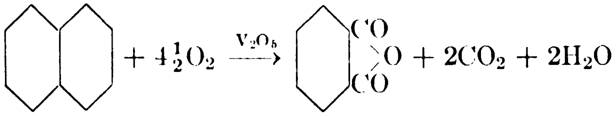
PHTHALIC ANHYDRIDE



From Naphthalene



Reaction



70–80% yield

Material Requirements

Basis—1 ton phthalic anhydride

Naphthalene (78°)	2,500 lb
Air	830,000 cu ft at 60°F

Process

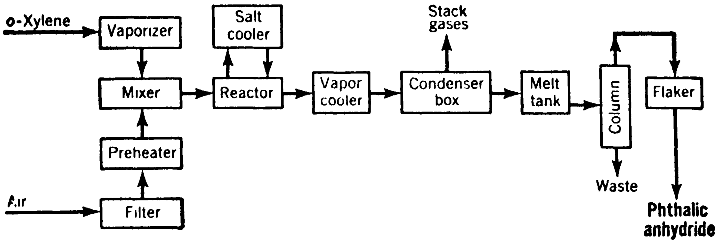
Naphthalene is melted and pumped to a vaporizer, where it is vaporized by bubbling primary preheated air through the molten material. Additional (secondary) air is added to the primary air–naphthalene vapor stream in a mixing section in the exit pipe from the vaporizer to bring the air–naphthalene ratio to 25 to 1 by weight. This vapor mixture is then led to a converter, consisting of multiple tubes filled with supported vanadium pentoxide catalyst. Heat (8,000 to 10,000 Btu per lb of naphthalene) is removed from the outside of the fixed catalyst, either by boiling mercury under suitable pressure or by pumping molten salt across the tube bank. In the converter the naphthalene is oxidized to phthalic anhydride, carbon dioxide, and water (temperature, 675 to 850°F; contact time, 0.1 sec).

Exit gases pass through a vapor cooler, which reduces the gas temperature to just above the dew point (about 260°F), and then enter large air-cooled condensers, which are boxlike compartments where crude phthalic anhydride crystallizes on the walls. The crude product is withdrawn from the condenser boxes and fed to a stainless-steel vacuum still for purification by distillation. The purified phthalic anhydride is usually melted and flaked for storage and packaging. Maleic anhydride, formed as a by-product, may be removed by working up the crystals in the last compartment of the condenser box system or by scrubbing the tail gases from the condenser boxes. Most commercial phthalic anhydride contains 0.25 to 0.40 per cent maleic anhydride.

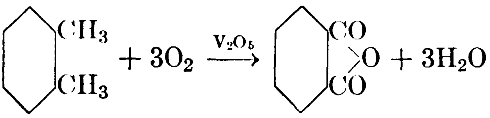
The vanadium pentoxide catalyst possesses a long life, acting satisfactorily for several years of continuous operation. The amount of phthalic anhydride produced is at least 20,000 times the weight of the catalyst present before reactivation is necessitated.

Phthalic anhydride is also produced, using a fluid catalyst consisting of very finely powdered vanadium pentoxide. The reactor containing the catalyst is heated to the proper operating temperature (using air preheated to 900°F), which is several hundred degrees lower than the temperature of the fixed catalytic bed. Molten naphthalene is introduced into the reactor and is vaporized by direct contact with the catalyst charge. The vapors become admixed immediately with the air–catalyst mixture, owing to the severely agitated nature of the catalyst bed. The air–naphthalene vapor mixture passes upward through the bed, and the naphthalene is converted to phthalic anhydride, carbon dioxide, carbon monoxide, and water vapor. The reaction gases, after leaving the dense catalyst phase, pass through a settling zone and into an internal cyclone system for removal of most of the catalyst. The vapors containing a small amount of catalyst dust are cooled and then passed through a catalyst-recovery system consisting of a series of specially designed filters. There is reported a 100 per cent recovery of catalyst with no poisoning, so that it is unnecessary to replenish the catalyst at any time. About 25 lb catalyst is required in the reactor per lb naphthalene fed per hr. The product gases contain crude phthalic anhydride, which is recovered in the manner described. The contact time is 10 sec, the air–naphthalene ratio about 10 to 1 by weight, and the yield of 99 per cent phthalic anhydride is better than 65 per cent.

From Orthoxylene



Reaction



70–80% yield

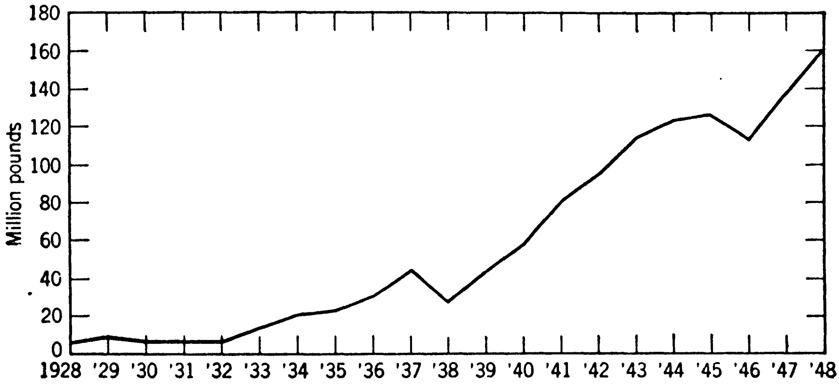
Material Requirements

Basis—1 ton phthalic anhydride

Orthoxylene	1,950 lb
Air	744,000 cu ft at 60°F

Process

Orthoxylene is vaporized and mixed with preheated air. About ten times the theoretical requirement of air is used in order to avoid operating within the explosive limits. The mixture is then fed into the reactor, which is similar to the one described previously for the oxidation of naphthalene. A vanadium pentoxide base catalyst is used, and the heat of reaction is removed by circulating molten salt outside the catalyst



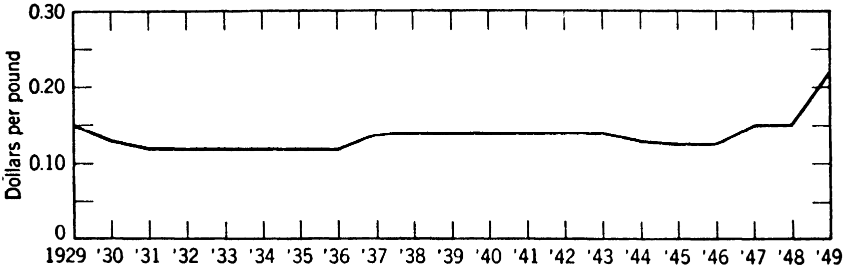
Production—Phthalic Anhydride

tubes. The conversion temperature is greater than 1,000°F, and the contact time is less than 1 sec.

The reaction gases, consisting of phthalic anhydride, carbon dioxide, and water, are cooled in heat exchangers, condensed, distilled, flaked, and packaged, in a manner similar to the purification of the naphthalene oxidation reaction product. The finished material is of high purity, analyzing about 99.7 per cent phthalic anhydride.

Use Pattern

	1947 (est.), per cent
Resins	55
Plasticizers	30
Dyestuffs	10
Miscellaneous	5
	100



Price—Phthalic Anhydride

Miscellaneous

Properties. Translucent, white crystalline flakes or needles; characteristic odor.

Mol. wt.	148.11	M.P.	130.8°C
Sp. gr.	1.527 at 4°C	B.P.	284.5°C

Very slightly soluble in cold water, soluble in alcohol, and slightly soluble in ether and hot water. Sublimes below its boiling point.

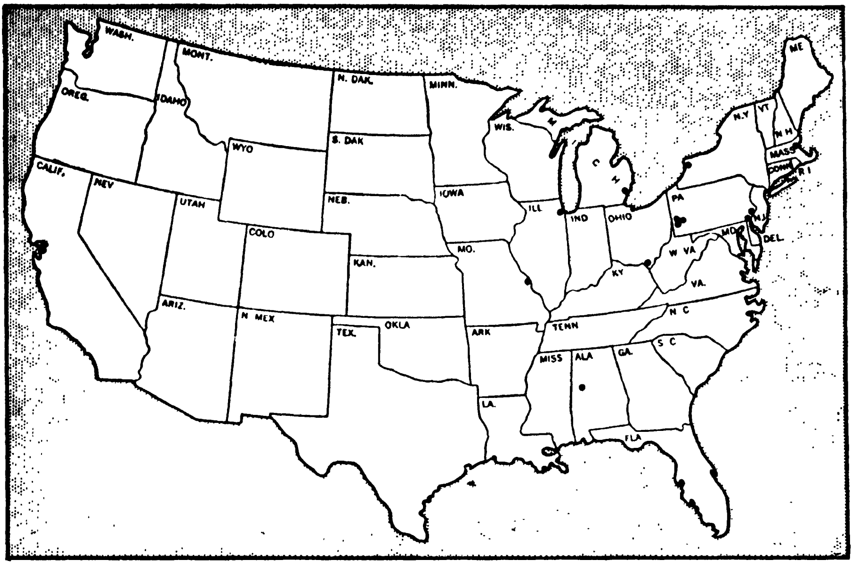
Flash point (closed cup)	305°F
Vapor density (air = 1)	5.10

Grades. Technical (99.0 to 99.8 per cent); pure (99.9 per cent).

Containers and Regulations. Barrels (80 to 250 lb), kegs (100 lb), paper bags (80 lb), and bottles. No ICC shipping label required.

Economic Aspects

Phthalic anhydride is another synthetic organic chemical based on the by-product coke industry. The sole raw material has always been naphthalene, but recently one plant has been built that uses orthoxylene from petroleum as the raw material. Orthoxylene is separated from its isomers in a 100-plate fractionating column. The distillation operation is said to be made economically feasible by the increased value of the meta-para fraction in aviation gasoline, in which orthoxylene is detrimental. The raw material fed to the phthalic anhydride plant is only 85 to 90 per cent orthoxylene, and the 10 to 15 per cent meta-paraxylene is oxidized to carbon dioxide and water. It is apparent, of course, that the use of pure orthoxylene would increase plant production considerably, because of less heat removal from the converters.



Location of Phthalic Anhydride Plants

All manufacturers also produce other organic chemicals, and many manufacture various synthetic resins, which in one form or another use the major phthalic anhydride production. Increased demands for alkyd resins, phthalate esters for plasticizers (especially for vinyl resins), and insect repellents during World War II were responsible for large production increases, which will probably continue further.

Phthalic anhydride manufacture presents many difficulties because of explosion hazards, fires, and the like. Process details are changing rapidly as in all catalytic developments, and considerable change can be expected in the future.

One recently constructed plant makes use of the fluid-catalyst technique developed by the petroleum industry. Reputed advantages of the process are better control of the oxidation reaction and direct production of phthalic anhydride, not requiring further purification.

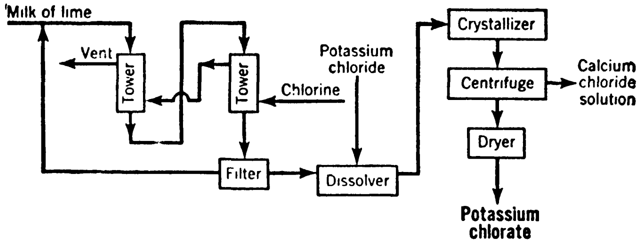
By-products of phthalic anhydride production are about 3 to 5 per cent maleic anhydride based on phthalic anhydride produced, and some quinones. The former is usually recovered, and suggestions have been made that in some cases it might be advisable to develop catalysts capable of producing larger quantities of maleic anhydride (see *Maleic Anhydride*).

A normal-sized plant has an annual capacity of 10,000,000 to 20,000,000 lb per yr; a small plant would be one producing 3,000,000 lb annually. Capital investment for the former approximates 10 to 11 cents per pound annual capacity. One plant has a capacity of more than 50,000,000 lb per yr.

POTASSIUM CHLORATE

$KClO_3$

From Calcium Chlorate



Reaction

$$6Ca(OH)_2 + 6Cl_2 \rightarrow Ca(ClO_3)_2 + 5CaCl_2 + 6H_2O$$

$$Ca(ClO_3)_2 + 2KCl \rightarrow 2KClO_3 + CaCl_2$$

85–95% yield

Material Requirements

Basis—1 ton potassium chlorate

Lime (96% CaO)	4,000 lb
Chlorine	4,320 lb
Potassium chloride (98%)	1,400 lb

Process

Potassium chlorate is produced by the double decomposition reaction between potassium chloride and calcium chlorate. The latter is made by the chlorination of milk of lime.

Quicklime (calcium oxide) is slaked with excess water to form milk of lime (calcium hydroxide). This aqueous suspension is charged into the first of a series of chlorinating towers or closed agitated tanks. Chlorine is introduced into the last tower and passes countercurrent to the lime flow. The chlorine is absorbed in the towers (except the last) to form calcium hypochlorite, $Ca(OCl)_2$. In the towers the temperature is maintained above 40°C (preventing the formation of insoluble basic compounds), but below 55°C (to prevent undue decomposition with loss of oxygen). The partially chlorinated product flows into the last tower, where at about 70°C the solution is overchlorinated, resulting in the conversion of hypochlorite to calcium chlorate.

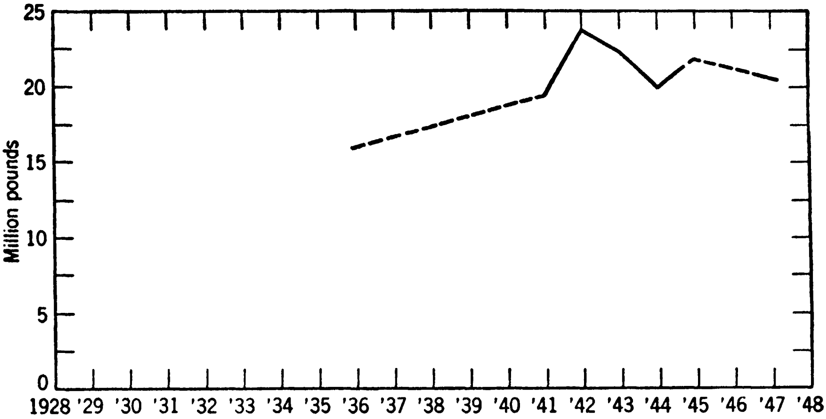
The chlorinated product is discharged from the last tower and passed through a filter to remove unreacted lime. The filter cake may be reused. The filtrate, containing 12 to 15 per cent calcium chlorate and less than 1 per cent hypochlorite, is run into an aluminum dissolving kettle, where pulverized potassium chloride is added in slight excess. The chloride dissolves in the hot chlorate liquor, and a double decomposition reaction takes place. The solution, containing principally potassium chlorate and calcium chloride, is discharged into a crystallizer, where it is cooled by artificial refrigeration (brine). Crude potassium chlorate crystallizes out and is recovered by centrifuging. The crude crystals may be recrystallized to yield purified potassium chlorate. The centrifuged product is dried in rotary dryers and ground to the correct mesh size. A yield of about 95 per cent of calcium chlorate is realized based on the lime used. The over-all yield of potassium chlorate from lime is 85 to 90 per cent.

Potassium chlorate may also be produced by direct electrolysis of a saturated solution of potassium chloride. The electrolysis is practically identical with that used in the production of sodium chlorate. See *Sodium Chlorate* for details.

The method of recovery of the chlorate from the cell liquor differs, however, because of the decreased solubility of potassium chlorate in water. The cell liquor is passed directly into a brine-cooled crystallizer where, on chilling, crystals of potassium chlorate form. The product is centrifuged, washed, and dried before packaging.

The sparingly soluble potassium chlorate crystallizes from solution during electrolysis, resulting in operational difficulties of the cells. It is best, therefore, to prepare sodium chlorate by electrolysis and obtain the potassium chlorate by the double decomposition reaction with potassium chloride. This operation is similar to the one described previously, using calcium chlorate. The sodium chlorate liquor is saturated with potassium chloride, concentrated in an evaporator, and cooled to yield potassium chlorate crystals. The crystals are centrifuged, washed, dried, and pulverized. The mother liquor is purged of sulfate ions and returned to the cells, after being brought to the proper concentration. The liquor is periodically debrominated and purged of sodium chloride by evaporation.

Potassium perchlorate, ($KClO_4$) is usually produced by the previously described reaction using sodium perchlorate and potassium

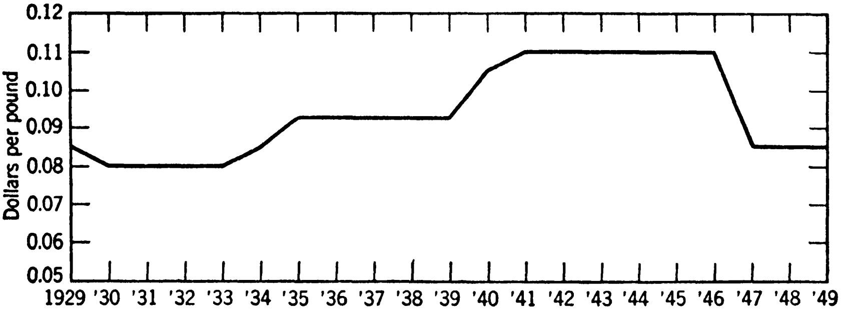


Production—Potassium Chlorate

chloride. For the manufacture of sodium perchlorate, see *Sodium Chlorate*.

Use Pattern

	Per cent
Matches	70
Explosives and miscellaneous	30
	100



Price—Potassium Chlorate

Miscellaneous

Properties. Transparent, colorless monoclinic crystals or white powder with a cooling, saline taste. Poisonous. Must not be mixed with combustible substances, such as sugar or sulfur, as explosions may result.

Mol. wt.	122.56	M.P.	368°C
Sp. gr.	2.32	B.P.	Decomposes at 400°C, giving off oxygen

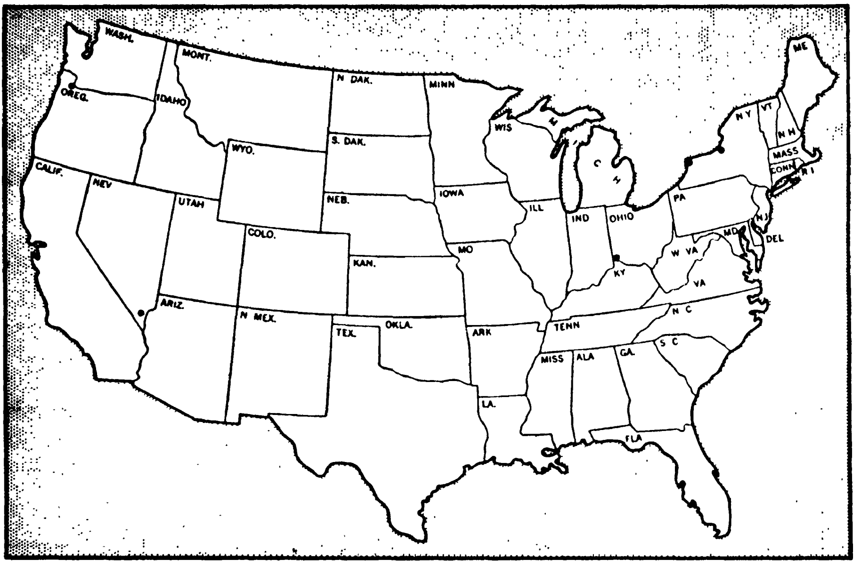
Soluble in water (3.3 g per 100 g at 0°C, 57 g per 100 g at 100°C), and alkalies. Very slightly soluble in alcohol (0.83 per cent).

Grades. Commercial, C.P., USP, pure granulated, and highest purity.

Containers and Regulations. Barrels, kegs, boxes, and bottles. Yellow ICC shipping label required.

Economic Aspects

Whether potassium chlorate is made electrolytically or chemically depends largely on other products made by a particular manufacturer. If potassium chlorate were the sole product manufactured, which is rarely the case, electrolysis of potassium chloride would be the simplest procedure. Usually, however, the potassium chlorate manufacturer also makes sodium chlorate, in which case potassium chlorate production is met by treatment of sodium chlorate cell liquors with potassium chloride. As with sodium chlorate (see *Sodium Chlorate*), either procedure demands low-cost power, since the process is based one way or another on an electrolytic process.



Location of Potassium Chlorate Plants

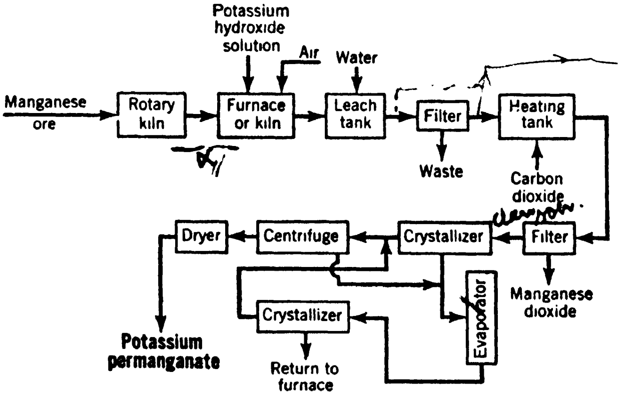
Potassium chlorate plants are generally smaller than sodium chlorate plants (1,000,000 to 4,000,000 lb per yr), since the latter must furnish requirements for both chemicals. A straight electrolytic plant probably costs approximately the same as a sodium chlorate plant, whereas a plant producing both chlorates requires a slight added investment for potassium chlorate recovery.

Potassium chlorate is also similar to sodium chlorate economically in that it too has one large principal use: in this case, in the manufacture of matches. The demand for potassium chlorate for various uses is fairly steady and uniform, and the only change that may occur in the future will depend on demands for the perchlorate in jet propulsion.

POTASSIUM PERMANGANATE

$KMnO_4$

From Manganese Ore



Reaction

$$MnO_2 + 2KOH + \tfrac{1}{2}O_2 \rightarrow K_2MnO_4 + H_2O$$

$$3K_2MnO_4 + 2CO_2 \rightarrow 2KMnO_4 + 2K_2CO_3 + MnO_2$$

55–88% yield

Material Requirements

Basis—1 ton potassium permanganate

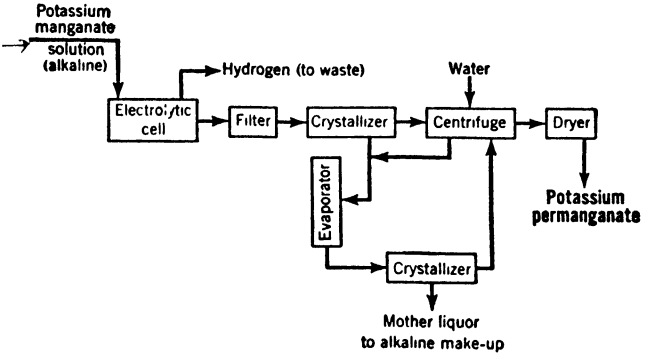
Manganese ore (88% MnO_2)	1,700 lb	Carbon dioxide	1,300 lb
Potassium hydroxide (100%)	1,000 lb	Lime	Depends on silica content of ore
Air	Variable		

Process

Manganese ore (85 to 90 per cent MnO_2) is calcined in a rotary kiln and then fed to a muffle furnace or another rotary kiln, where it is allowed to react with caustic potash (50 per cent solution in 25 per cent excess) and air at 300°C to produce potassium manganate (K_2MnO_4).

If silica is present in the original ore, quicklime is added to remove the silica. The product of the furnace is leached, and the resulting solution is filtered. The manganate solution is then heated and converted to a permanganate solution by contact with carbon dioxide gas. The resulting solution is filtered hot to remove manganese dioxide, which may be re-used by mixing with ore. The clarified solution is cooled, and potassium permanganate crystals are formed. The crystals are centrifuged, washed, and dried in conventional equipment. The mother liquor and centrifugal wash liquors are pumped to double-effect evaporators and evaporated to saturation, after which the liquor is sent through a second crystallization cycle. The second mother liquor may be added to the potassium hydroxide make-up tank and returned to the furnace.

From Potassium Manganate by Electrochemical Oxidation



Reaction

$$2K^+ + MnO_4^{=} + H_2O \rightarrow K^+ + MnO_4^- + KOH + \tfrac{1}{2}H_2 \quad \text{or}$$

$$2K_2MnO_4 + 2H_2O \rightarrow 2KMnO_4 + 2KOH + H_2$$

80–90% yield; 70% current efficiency

Material Requirements

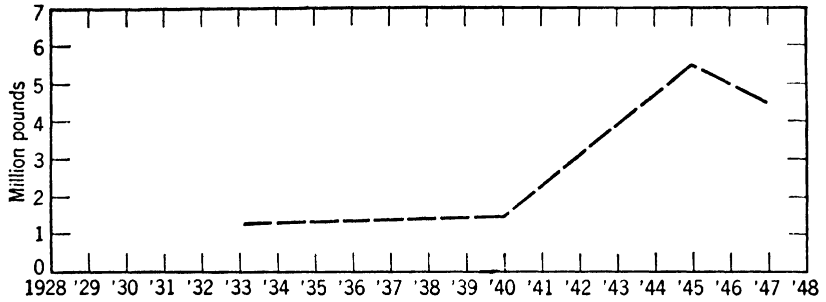
Basis—1 ton potassium permanganate

Manganese ore (88% MnO_2)	1,700 lb	Lime	Depends on silica content of ore
Potassium hydroxide (100%)	1,000 lb	Electricity	640 kw-hr
Air	Variable		

Process

Potassium manganate solution, prepared as in the chemical process described previously, is adjusted to about 9 per cent potassium manganate and 5 per cent potassium hydroxide and fed to an electrolytic cell. The cell consists of a steel tank with sheet-iron or iron-net anodes, iron rod cathodes, and no diaphragm. Good agitation is required and is obtained in one type of cell by rotation of an iron-net anode through which the solution flows. The operating characteristics of a typical cell are: temperature, 60°C; anode current density, 84 amperes per square foot; cathode current density, 840 amperes per square foot; potential drop per cell, 3 volts. During the oxidation, potassium permanganate crystallizes, the cell liquor becomes more alkaline, and hydrogen is evolved at the cathode. The hydrogen is usually not recovered.

The cell effluent is cooled, and potassium permanganate crystallized as in the previously described process.

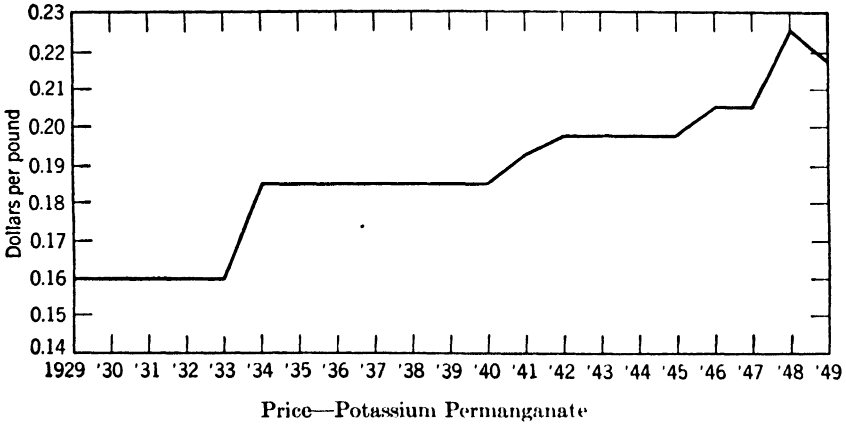


Production—Potassium Permanganate (Estimated)

Use Pattern

Chemical processing
Vitamin manufacture
Metal treating
Medicines and pharmaceuticals

No breakdown available



Price—Potassium Permanganate

Miscellaneous

Properties. Dark purple, rhombic crystals having a blue metallic sheen and a sweetish, astringent taste.

Mol. wt.	158.03	M.P.	Decomposes <240°C
Sp. gr.	2.703		

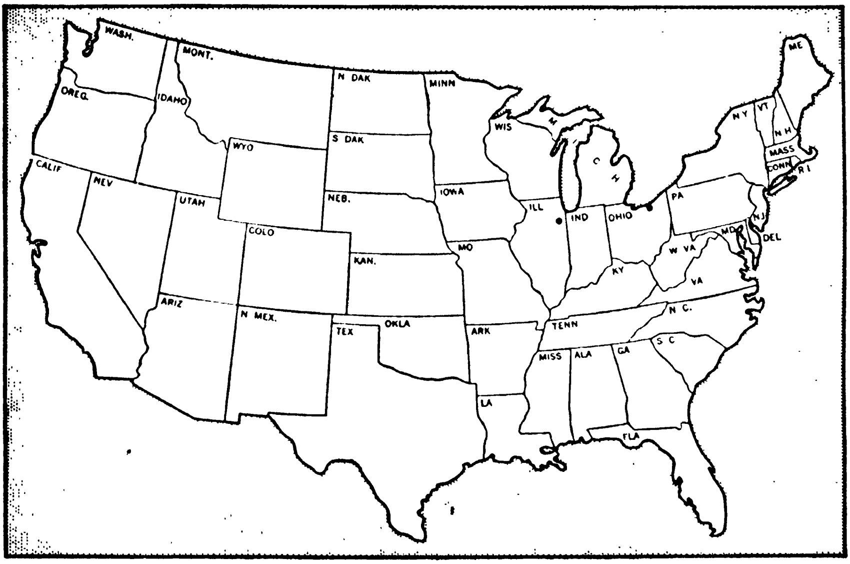
Soluble in water (2.83 g per 100 g at 0°C, 32.35 g per 100 g at 75°C), and sulfuric acid. Decomposes in alcohol.

Grades. Technical, USP, and C.P.

Containers and Regulations. Drums, kegs, boxes, cans, and bottles. Dangerous fire hazard, as explosions are prone to occur when it is brought in contact with organic and readily oxidizable materials either in solution or the dry state. Yellow ICC shipping label required.

Economic Aspects

Potassium permanganate is an interesting chemical, if for no other reason than that one company has built its business primarily around its production and supplies the bulk of the material to industry. Although it is a common inorganic preparation in most colleges and universities, economic production is very difficult because of the great care that must be taken to maintain yields and purity.



Location of Potassium Permanganate Plants

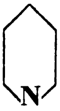
This problem is inherent in both the chemical and electrochemical processes, which appear to be roughly competitive. In both processes, careful control and intimate contact of reactants are necessary. In the extraction step, maximum yield and maximum purity call again for very careful control. The same problems occur throughout the process.

In the electrolytic process, chief variations are in cell design, electrode metal, liquor concentration, temperature, and so on. Current efficiencies are relatively low: 60 to 70 per cent. During World War II, two attempts were made to build and operate a small electrolytic plant in the United States, but neither was economically successful.

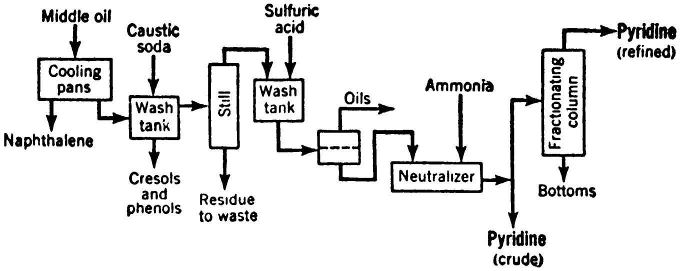
The principal raw material for permanganate manufacture is high-grade manganese ore, but suggestions have been made that under certain conditions it might be economic to utilize manganese dioxide sludge recovered from organic oxidation processes. The anodic solution of ferromanganese has also been tried on various-sized scales.

Since the chief use of potassium permanganate is as an oxidizing agent in organic-chemical preparations, and there only in relatively small amounts for a given process, demand may be expected to increase only slightly. In many cases, the cheaper sodium dichromate is equally as satisfactory.

PYRIDINE



From Coal Carbonization



Recovery

0.16 lb per ton of coal (33% volatile matter)

Process

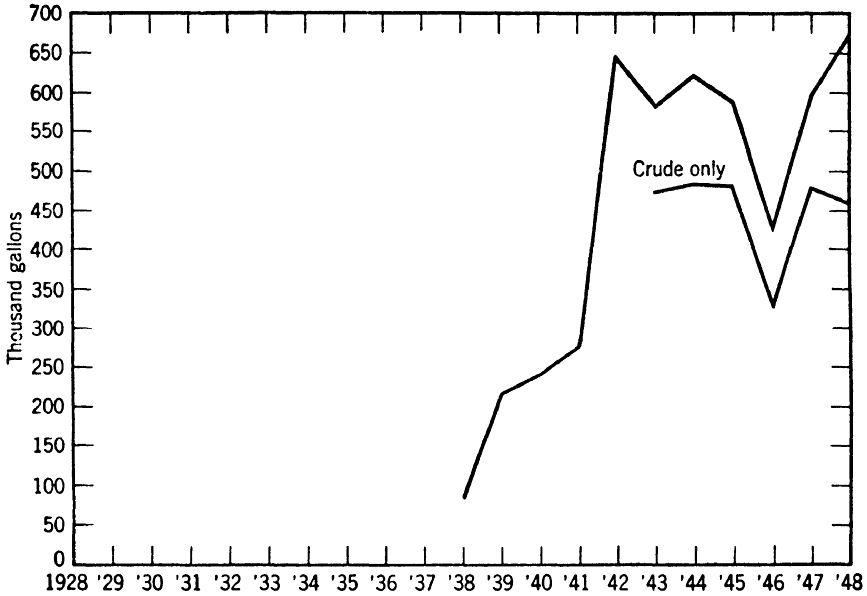
Pyridine is produced during the carbonization of coal and is recovered in the by-product coking process. The raw coal gas evolved from by-product coke ovens contains approximately 0.014 lb of total pyridine bases per 1,000 cu ft of gas. About 40 per cent of this material condenses out with the coal tar (using the indirect and semidirect ammonium sulfate systems); the remainder is carried along to the ammonia scrubbers or saturators. The pyridine base content of this gas (before entry into the saturator) is about 0.008 lb per cu ft of gas, which is equivalent to about 0.004 per cent by volume. In the recovery of ammonia from the gas, some of the pyridine is absorbed, constituting an impurity in the aqueous ammonia or ammonium sulfate (see *Ammonia* and *Ammonium Sulfate*). The remaining pyridine bases are absorbed in the light oil, provided no provisions are made to remove them previously. See *Coke* for details on by-product coking and sequence of tar, ammonia, and light-oil-recovery operations. Of the total pyridine bases in the crude coke-oven gas, approximately 70 per cent is pyridine; the remainder is a mixture of various alkylated pyridines and other basic materials such as the picolines, lutidines, collidines, and quinolines. Pyridine is recovered both at the coke plant (in conjunction with ammonia absorption) and at the tar distillers' plant (from the middle-oil distillate). The latter, the older and easier method of recovery, operates as follows:

The crude coal tar obtained from the tar separators in the by-product coking plant (see *Coke*) is distilled in pipe stills and fractionated to yield a fraction known as middle oil (see *Naphthalene*). The middle oils (also called creosote oils) are cooled to crystallize naphthalene and are then sent to wash tanks. Here the oil is washed with caustic soda to remove the tar acids (see *Cresol* and *Phenol*). The middle oil (now known as neutral oil), with most of the naphthalene and tar acids removed, is then distilled. The distillate is charged into acid wash tanks, where the crude pyridine bases are extracted with sulfuric acid (or sometimes hydrochloric acid). The extract, which consists of water-soluble pyridine sulfates, is separated from the nonaqueous oils by decantation. The decanted solution may be steamed to volatilize any dissolved oils (if necessary), or it may be charged directly into neutralizing tanks. Here the crude pyridine bases are regenerated, using either caustic soda or ammonia solution. The crude pyridine is dried, either over caustic soda or by azeotropic distillation with benzene. The crude product may be purified by fractional distillation to yield refined pyridine.

As mentioned previously, about 60 per cent of the total pyridine bases originally present in the coke-oven gases pass through the tar condensers into the ammonia-recovery system. In the past, these bases were not recovered, owing to the adequate supply of pyridine, which was more easily and cheaply obtained from the tar. However, since the war, increased consumption of pyridine has made it feasible to recover it from the coal gas. This recovery is best accomplished in the operation of the ammonia saturator. See *Ammonium Sulfate* for operational details.

In the semidirect ammonium sulfate process, the coal gases (after most of the tar has been removed) are bubbled through dilute sulfuric acid to form ammonium sulfate. The crystalline sulfate is allowed to drain on a table before centrifuging. The mother liquor from the tables contains 2 to 6 per cent pyridine in the form of pyridine sulfates. One process for their recovery involves the neutralization of the liquor with ammonia to liberate the pyridine bases. The saturator liquor is charged continuously into a neutralizing still, where it is "steam-distilled" with ammonia vapors from an ammonia still. The effluent from the neutralizer is adjusted to 6 to 7 *p*H and is returned to the saturator. The vapors pass through a reflux condenser maintained at 92 to 96°C to another condenser. The condensate passes to a decanter where the two layers that form are separated. The lower layer, a strong solution of ammonium carbonate, is discharged into the ammonia-liquor system. The upper layer, containing the pyridine bases, is decanted into crude pyridine storage tanks. The crude material contains about 15 per cent water, which may be removed by azeotropic distillation or desiccation.

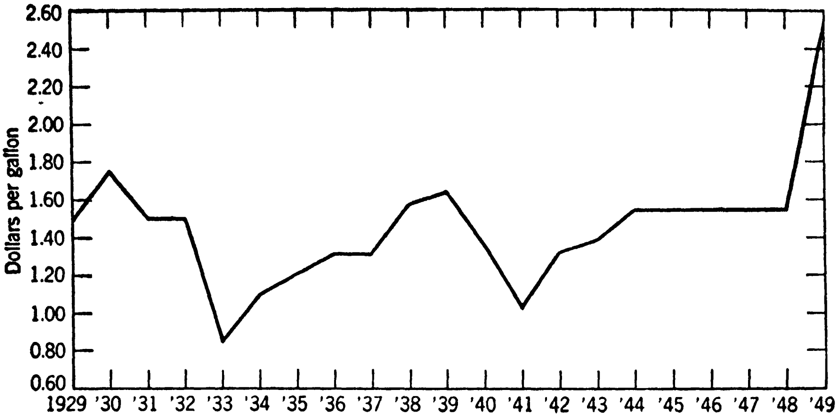
The crude bases may be refined by fractional distillation. After the water has been removed, approximately 69 per cent of the crude material will distil at 115°C to yield refined pyridine. The remainder of the crude material may be distilled to yield the next fraction, consisting of a mixture of picolines, lutidines, and collidines (about 8 per cent). About 4 per cent aniline may then be removed to leave a residue containing about 12 per cent quinoline bases.



Production—Pyridine (Crude and refined)

Use Pattern

	1947 (est.), per cent
Vitamins	40
Sulfa drugs	20
Rubber chemicals	10
Miscellaneous	30
	100



Price—Pyridine, Denaturing Grade

Miscellaneous

Properties. Colorless to slightly yellowish liquid with a sharp, penetrating, empyreumatic odor and a burning taste.

Mol. wt.	79.10	M.P.	−42°C
Sp. gr.	0.982 20°C/4	B.P.	115.5°C

Weight per gallon 8.19 lb (20°C)

Soluble in water, alcohol, ether, benzene, petroleum ether, and fatty oils.

Flash point (closed cup)	68°F
Ignition temperature	900°F
Vapor density (air = 1)	2.73
Explosive limits (% by volume in air)	Lower 1.8
	Upper 12.5

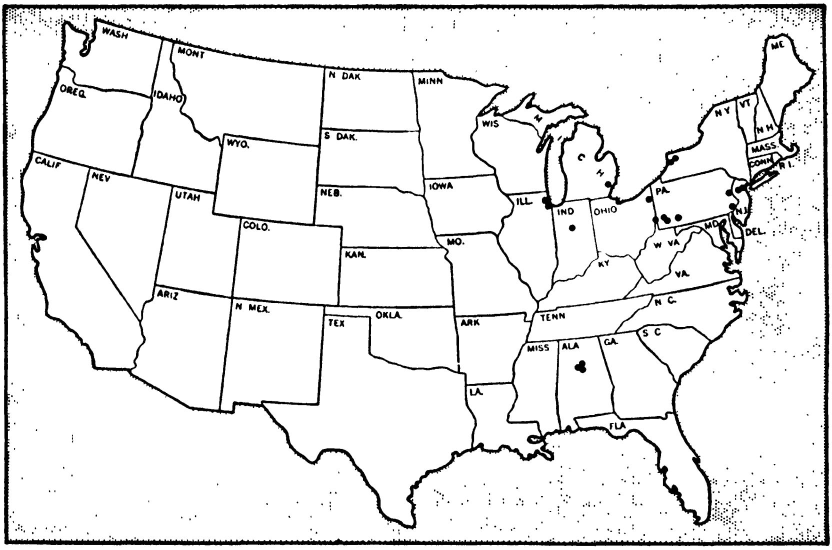
Grades. Technical, medicinal, and C.P.

Containers and Regulations. Drums, barrels, cans, and bottles. Red ICC shipping label required.

Economic Aspects

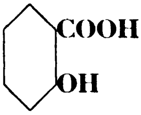
Pyridine and its homologs (the picolines and lutidines) are minor constituents of coal tar and raw coke-oven gas that have not always been worth recovering. The pyridine bases have been known and used to a small extent ever since the advent of by-product coking, but only recently have they, particularly pyridine, become important to industry. Three new products, sulfapyridine, zelan, and the vitamin, niacin, all require pyridine as a raw material and have been largely responsible for increase in production. One effect of this demand has been the replacement of pyridine by high-boiling tar bases in the manufacture of rust inhibitors, a former major outlet for pyridine. Another comparatively new and important use for pyridine is in the manufacture of pyridylmercuric esters, which have excellent fungicidal properties.

Toward the end of World War II it was proposed to use vinyl pyridine as a partial substitute for styrene in the manufacture of synthetic rubber, because of improvements in the characteristics of the elastomer with a partial vinyl pyridine substitution. It is understood that the product was not so satisfactory as was first thought, but the thought arises that a market of this size for pyridine would greatly strain the facilities of the coal-tar industry and would probably initiate a search for synthetic pyridine. On the other hand, the thermal or catalytic cracking of nitrogen-containing petroleum bases, or the higher tar bases, might be made to yield adequate quantities of pyridine. Certain crude naphtha-acid extracts also could be worked up for pyridine recovery.

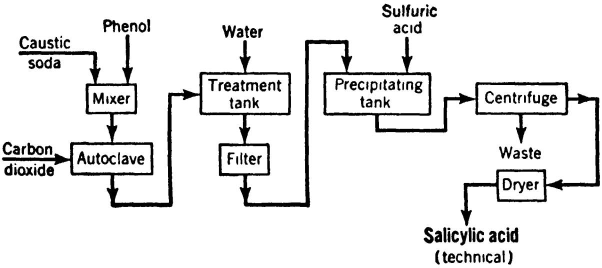


Location of Pyridine Plants

SALICYLIC ACID



From Phenol



Reaction

$$C_6H_5OH + NaOH \rightarrow C_6H_5ONa + H_2O$$

$$C_6H_5ONa + CO_2 \rightarrow HOC_6H_4COONa$$

$$2HOC_6H_4COONa + H_2SO_4 \rightarrow 2HOC_6H_4COOH + Na_2SO_4$$

85–90% yield

Material Requirements

Basis—1 ton salicylic acid

Phenol	1,600 lb	Carbon dioxide	1,000 lb
Caustic soda	690 lb	Sulfuric acid	900 lb

Process

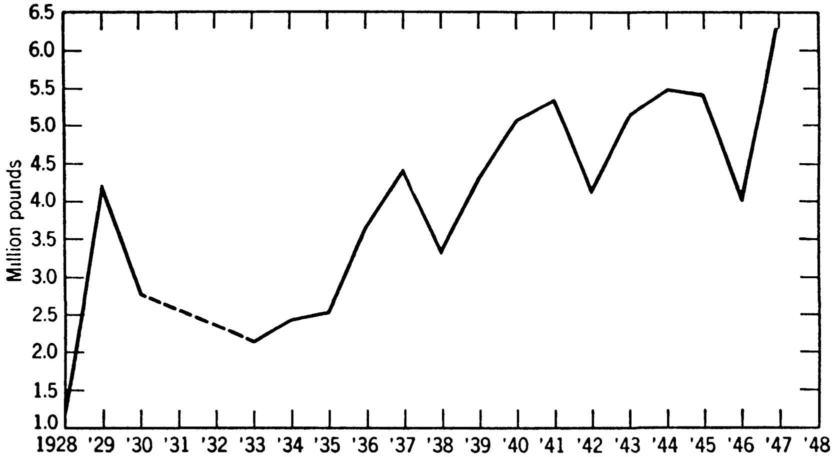
Phenol is run into an equimolar amount of hot aqueous caustic soda in mixers. The resulting solution is heated to about 130°C and evaporated to dryness in stirred autoclaves under vacuum. This operation is sometimes carried on in heated ball mills to insure dryness as well as grinding of the resulting sodium phenate. After drying, the temperature is reduced to about 100°C, and dry carbon dioxide gas is introduced under about 6 atm (90 to 100 psi) pressure. After the desired amount of carbon dioxide is absorbed, the charge is generally heated at 150 to 170°C for several hours.

The crude autoclave product, after cooling, is dissolved in about an equal amount of water and filtered. It may be precipitated with acid and dried or purified in one of two ways before the precipitation. Contamination with iron must be avoided in these operations.

One method consists of decolorizing the crude sodium salicylate solution with activated carbon containing zinc dust. After filtering, the clear, almost colorless solution is acidified with an excess of sulfuric or hydrochloric acid. The precipitated salicylic acid is centrifuged and dried in rotary dryers to give a high grade of salicylic acid.

The crude sodium salicylate solution may also be purified by crystallization in the form of its hexahydrate ($C_7H_5O_3Na \cdot 6H_2O$). At a temperature below 20°C, the hexahydrate crystallizes out after seeding, leaving many impurities behind. The crystals are separated from the mother liquor by centrifuging and washed with small amounts of cold water to remove adherent mother liquor. This material may be recrystallized to yield USP sodium salicylate, or it may be acidified and precipitated as described previously, to give a very good grade of acid.

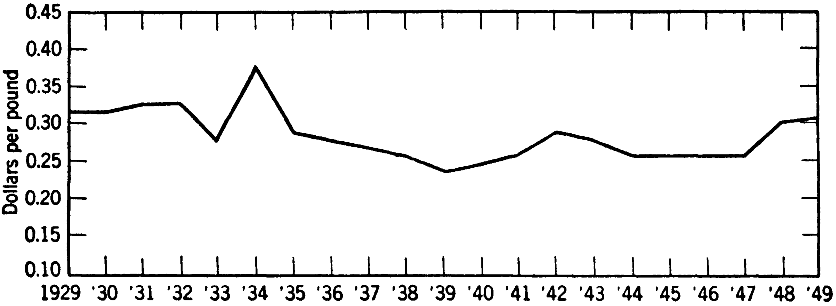
USP salicylic acid is generally obtained by subliming the technical acid prepared as outlined previously.



Production—Salicylic Acid (USP)

Use Pattern

	Per cent
Aspirin (acetyl salicylic acid)	65
Other medicinals (including methyl salicylate)	25
Miscellaneous (including dyes)	10
	100



Price—Salicylic Acid

Miscellaneous

Properties. White needles or crystalline powder.

Mol. wt.	138.12	M.P.	159°C, sublimes at 76°C
Sp. gr.	1.443 20°C/4	B.P.	211°C (20 mm Hg)

Very slightly soluble in water (0.16 g per 100 g at 4°C, 2.6 g per 100 g at 75°C). Soluble in alcohol (49.6 g per 100 g at 15°C), ether (50.5 g per 100 g at 15°C), acetone, oil, and turpentine.

Grades. Technical (*ca.* 98 to 99 per cent) and USP (99.5 per cent minimum).

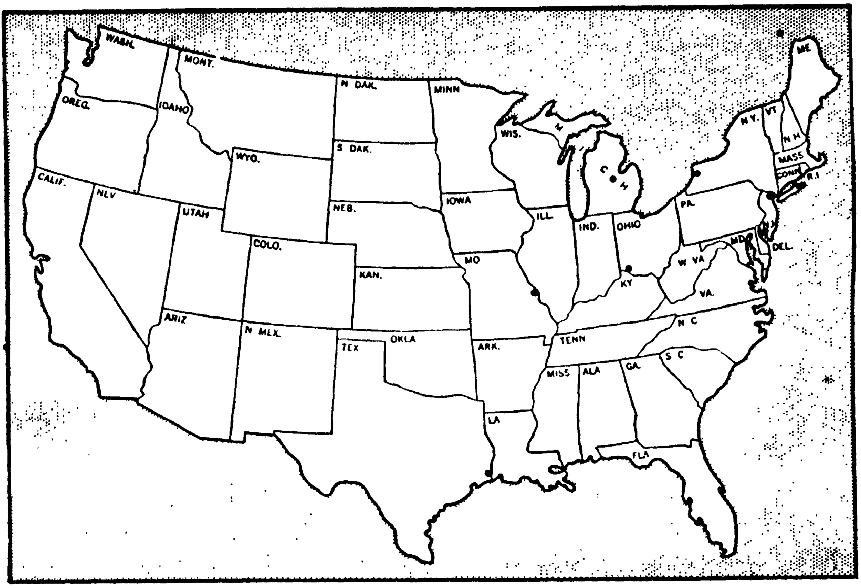
Containers and Regulations. Barrels (100 to 150 lb), kegs, fiber drums and cartons, and bottles of various smaller sizes. ICC shipping label not required.

Economic Aspects

Salicylic acid is classified as a fine chemical and is used almost exclusively as a medicinal or as an intermediate in the manufacture of medicinals and pharmaceuticals. Actually, salicylic acid and its derivatives account for about one-half the total amount of coal-tar medicinals produced in the United States, chiefly because of the enormous sale of aspirin (acetyl salicylic acid). Salicylic acid is usually manufactured by makers of phenol, the chief raw material, who engage in a general line of fine-chemicals manufacture. Aspirin, the chief product of which salicylic acid is the intermediate, is also commonly manufactured by the same producers, who sell it in bulk to pharmaceutical houses, which tablet and package it for sale.

A good-sized plant has a capacity of 4,000,000 to 6,000,000 lb salicylic acid per year. Such a plant costs about $1,250,000.

Any future expansion of the industry will depend on wider use of the various pharmaceuticals derived from salicylic acid. The amounts used for dyes probably will not increase greatly.

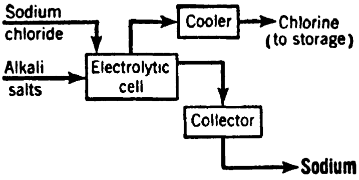


Location of Salicylic-Acid Plants

SODIUM

Na

From Salt by Electrolysis



Reaction

$$2NaCl \rightarrow 2Na + Cl_2$$

75–85% current efficiency

Material and Utility Requirements

Basis—1 ton metallic sodium

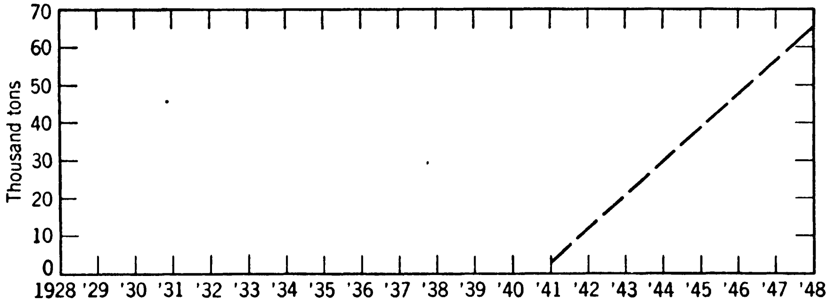
Sodium chloride	6,300 lb
Calcium chloride	12 lb
Electricity	15,000 kw-hr

Process

Common salt (NaCl, M.P. 804°C) is mixed with sufficient amounts of alkali fluorides and calcium chloride, to lower the fusion point of the salt to 600°C, and fused in an electrolytic cell. The most common cell used, the Downs cell, is a closed rectangular refractory-lined steel box with separate anode and cathode compartments. The graphite or carbon anode enters the bottom of the cell; the cathode is an annular piece of iron or copper. A diaphragm of iron gauze separates the two compartments and extends upward into a ceramic collecting dome connected to a ceramic duct, through which chlorine formed at the anode is led to compressors. Molten sodium, liberated at the cathode, is guided by the double-annular diaphragm into a pipe, through which it rises and overflows into a collecting vessel, which protects the sodium from oxidation. The sodium is withdrawn from the bottom of the collecting vessel, filtered, and delivered to packaging. It is usually packaged in the form of 2.5- and 12-lb bricks. The cell is operated at 600°C and at a voltage drop of 7 to 8 volts per cell. The chlorine produced is dry and quite pure.

Once the cell is operating, salt is added to it periodically. It is not necessary to add the fusion-point-lowering salts, since they are fairly stable under the conditions of operation.

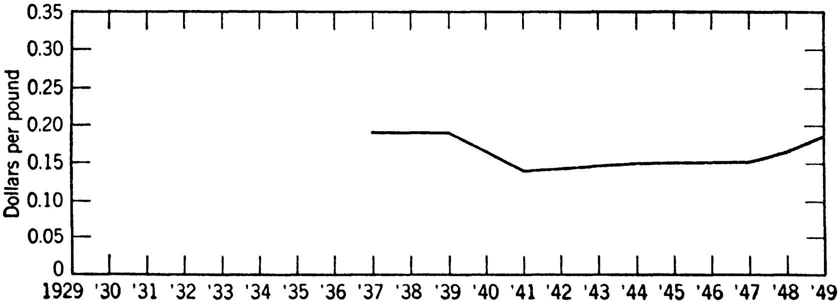
The Castner cell, in which sodium is made by the electrolysis of caustic soda, operates at 320 to 330°C. Other operating characteristics are: anode current density, 150 amperes per square decimeter; cathode current density, 200 amperes per square decimeter; current efficiency, 36 per cent; voltage drop per cell, 4.5 to 5.0 volts.



Production—Sodium (Estimated)

Use Pattern

	Per cent
Tetraethyl lead	50
Sodium derivatives (principally sodium cyanide and sodium peroxide)	40
Miscellaneous	10
	100



Price—Sodium

Miscellaneous

Properties. Light, soft, ductile, malleable silver-white metal, which oxidizes rapidly in air. At ordinary temperatures it is of waxlike consistency, but it becomes brittle at low temperatures.

Mol. wt.	22.997	M.P.	97.5°C
Sp. gr.	0.97 (20°C)	B.P.	880°C

Decomposes water, on contact, with vigorous evolution of hydrogen, forming sodium hydroxide. Dangerous fire hazard. Decomposes on contact with alcohol. Insoluble in benzene, petroleum ether, kerosene, and naphtha.

Grades. Technical (99.95 per cent).

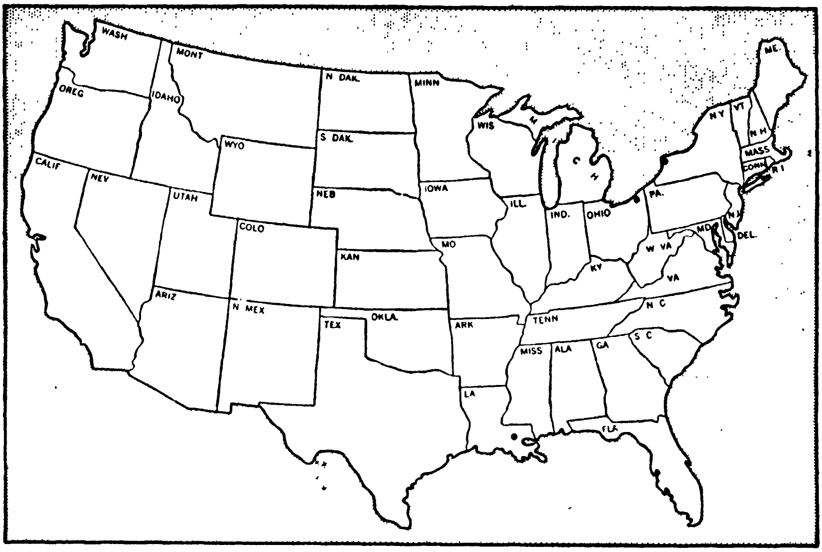
Containers and Regulations. Tank cars (special), drums, pails, tins in cases. Seldom shipped any more immersed in naphtha or similar liquids, but in special airtight containers. Yellow ICC shipping label required.

Economic Aspects

It is a surprise to many to learn that, except for iron, sodium is the cheapest metal on a volume basis. Its great reactivity, however, precludes its use as a structural material and enhances its value as a chemical. Although its main uses now are in the manufacture of tetraethyl lead and sodium cyanide, there is a distinct possibility that large amounts may be used in the future as electric conductors, since the cost of sodium on a conductance basis is lower than that of any other metal. Another new use, which shows promise of much greater utilization in the future, is in the descaling of metals by the sodium hydride process. There is also a strong promise of considerable use of sodium hydride as a catalyst in the Claisen condensation. On the other hand, development of a substitute for tetraethyl lead could materially affect sodium production, but, even so, future production of sodium will probably increase as proper handling methods become better known.

Originally, metallic sodium was made by chemical processes such as the distillation of mixtures of soda ash, coke, and lime, or caustic soda, iron carbide, and lime. These were replaced by the electrolysis of fused caustic soda, and the latter, in turn, has been largely displaced by the electrolysis of sodium chloride. The last-mentioned process is much more difficult technically than the electrolysis of caustic soda but offers the far greater advantage of a cheaper raw material. Although some sodium is still made by the electrolysis of caustic soda, all new installations use sodium chloride and incidentally produce chlorine as a by-product.

The Castner cell is used for the electrolysis of caustic soda and is quite small (its capacity is 250 lb molten sodium hydroxide). The Downs cell is the most commonly used of the sodium chloride cells. Plants in the range of 5,000,000 to 10,000,000 lb annually require an investment of approximately 30 cents per annual pound. A plant with an annual capacity of 36,000,000 lb is under construction and is expected to cost $10,000,000 (1950).



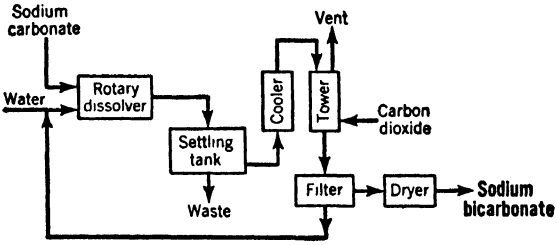
Location of Sodium Plants

SODIUM BICARBONATE

(BAKING SODA)

$NaHCO_3$

From Sodium Carbonate (Soda Ash)



Reaction

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3$$

90–95% yield

Material Requirements

Basis—1 ton sodium bicarbonate

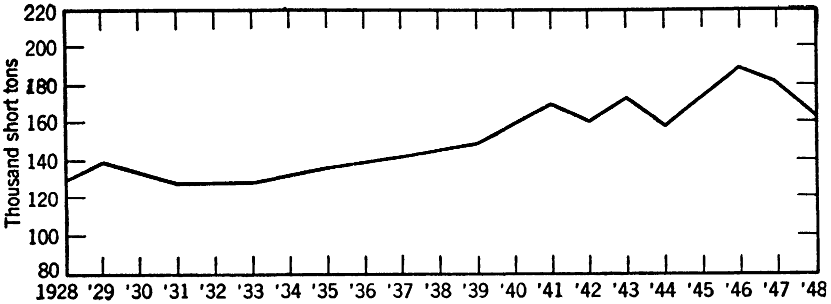
Sodium carbonate	1,380 lb
Carbon dioxide	600 lb

Process

Sodium bicarbonate, also known as bicarbonate of soda and baking soda, is produced by treating a saturated solution of sodium carbonate with carbon dioxide.

Sodium carbonate (soda ash) is charged with water into a rotary dissolver to make a saturated solution. The solution, after settling and cooling, is pumped to the top of a carbonating tower, which is similar to the tower used in the Solvay process for manufacturing sodium carbonate. Carbon dioxide is introduced into the bottom of the tower (maintained at about 40°C) by compressors.

The suspension of sodium bicarbonate formed is withdrawn from the bottom of the tower, filtered, and washed on a rotary drum filter. The filtrate is recycled to the rotary dissolver. The washed filter cake, which contains about 8 per cent moisture, is then dried on either a continuous belt conveyer (enclosed in a chamber) at 70°C or in a vertical tube dryer, in which the temperature of the hot air is maintained at 70 to 90°C. From the cyclones on the tube dryer, the bicarbonate is transported by a screw conveyer to the packing bins. Sodium bicarbonate of about 99.9 per cent purity is obtained in practically theoretical yield.

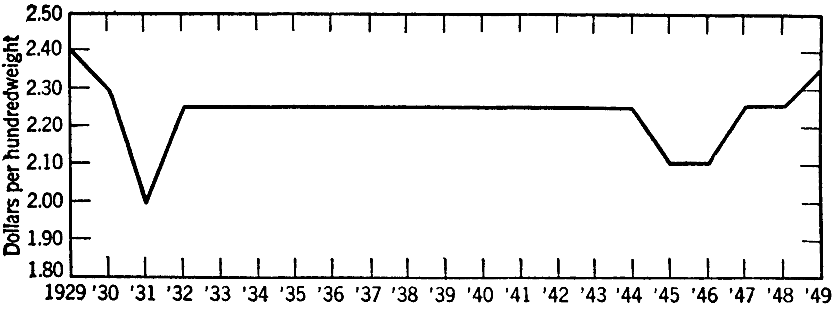


Production—Sodium Bicarbonate (Refined—100% $NaHCO_3$)

Use Pattern

Baking powders
Carbonated beverages
Leather goods
Fire extinguishers
Drugs
Miscellaneous

No breakdown available



Price—Sodium Bicarbonate

Miscellaneous

Properties. White monoclinic crystals or powder with a cooling, slightly alkaline taste.

Mol. wt.	84.01	M.P.	Loses CO_2 at 270°C
Sp. gr.	2.20		

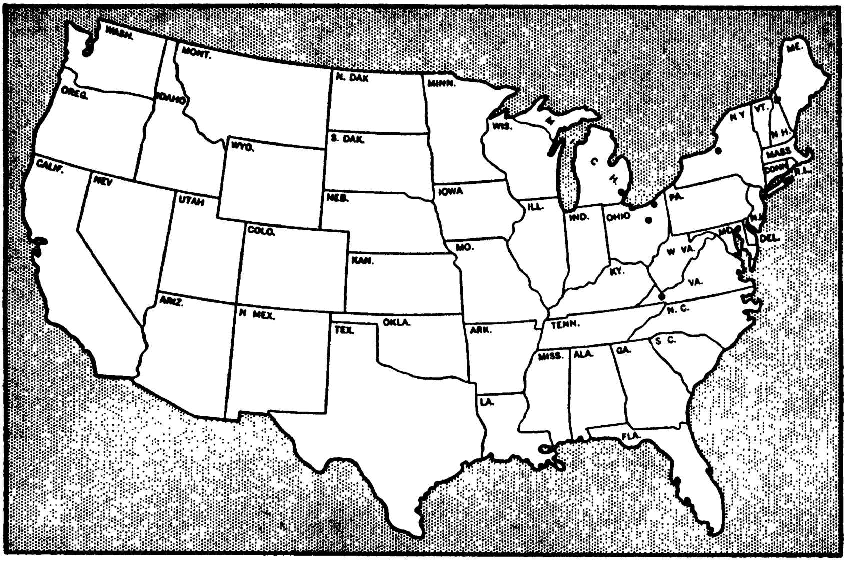
Soluble in water (6.9 g per 100 g at 0°C, 16.4 g per 100 g at 60°C). Insoluble in alcohol.

Grades. Commercial, C.P., USP, reagent, and highest purity.

Containers and Regulations. Barrels, bags, kegs, boxes, cartons, and bottles. No ICC shipping label required.

Economic Aspects

The manufacture of sodium bicarbonate (baking soda) is a typical example of those processes in which it is economically advantageous to purify the raw material in order to obtain a pure product, rather than to purify an impure end product. Accordingly, most sodium bicarbonate is made by converting soda ash rather than by purifying the intermediate sodium bicarbonate formed in the ammonia–soda process. Besides securing a higher-purity product, two other reasons are given for following the first-mentioned process. One is higher recovery of ammonia, and the other is that rich carbon dioxide gas may be recovered on calcining sodium bicarbonate, whereas only lean gas is needed to recarbonate soda ash. Some sodium bicarbonate is made, however, by purifying impure sodium bicarbonate.



Location of Sodium Bicarbonate Plants

The uses of sodium bicarbonate and, hence, the market for it appear to be stabilized, and no great changes may be expected in the future. Manufacture has been and probably will remain a minor function of soda-ash producers. Extra plant investment required for a soda-ash producer to manufacture sodium bicarbonate is usually small; part of it would be required in a soda-ash plant, whether or not bicarbonate were to be manufactured.

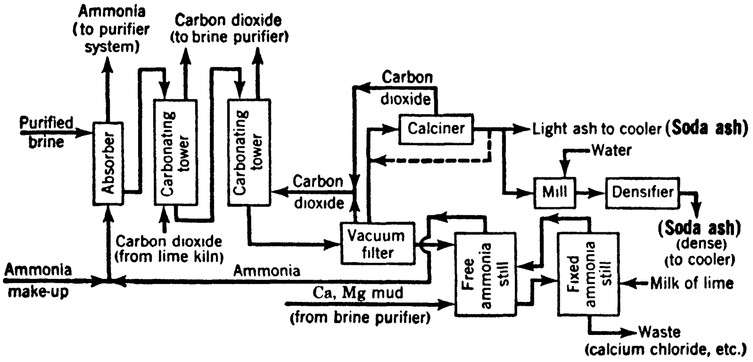
Those manufacturers making bicarbonate usually convert only about 2 per cent of soda ash manufactured to sodium bicarbonate.

SODIUM CARBONATE

(SODA ASH)

Na_2CO_3

By the Ammonia–Soda or Solvay Process


Ammonia (to purifier system)
Carbon dioxide (to brine purifier)
Purified brine
Absorber
Carbonating tower
Carbonating tower
Carbon dioxide
Calciner
Light ash to cooler (Soda ash)
Water
Mill
Densifier
(Soda ash) (dense) (to cooler)
Carbon dioxide
Vacuum filter
Free ammonia still
Fixed ammonia still
Milk of lime
Carbon dioxide (from lime kiln)
Ammonia make-up
Ammonia
Ca, Mg mud (from brine purifier)
Waste (calcium chloride, etc.)

Reaction

$$CaCO_3 \rightarrow CaO + CO_2 \qquad C + O_2 \rightarrow CO_2$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad NH_3 + H_2O \rightarrow NH_4OH$$

$$NH_4OH + CO_2 \rightarrow NH_4HCO_3$$

$$NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$$

$$2NaHCO_3 + \text{Heat} \rightarrow Na_2CO_3 + CO_2 + H_2O$$

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + H_2O$$

75% yield

Material and Utility Requirements

Basis—1 ton sodium carbonate (58%)

Salt	3,000 lb	Ammonia loss	6 lb [as $(NH_4)_2SO_4$]
Calcium carbonate (limestone)	2,400 lb	Carbon dioxide	1,100 cu ft
Coke	2,000 lb	Sodium sulfide	3 lb
Coal (boilers and dryers)	900 lb	Cooling water	16,000 gal

Process

Saturated salt brine (15°C) is purified in a series of absorbers with ammonia and carbon dioxide from waste process gases. Calcium, magnesium, and other heavy metal ions precipitate as a mud, which is removed in a series of settling tanks. Purified brine is then pumped to an internally cooled absorbing tower to pick up ammonia fed into the bottom of the absorber. Ammoniated brine leaving the absorber (80 g ammonia and 260 g sodium chloride per l) at 20 to 25°C is pumped to two carbonating towers in series, in which it first meets lean carbon dioxide gases from the kiln and then rich carbon dioxide from the bicarbonate calciner. Sodium bicarbonate is formed in the towers, and the slurry leaving the bottom of the second tower consists of sodium bicarbonate crystals (0.75 mole per mole of sodium chloride entering the system) and a solution of ammonium bicarbonate, ammonium chloride, unreacted sodium chloride, soluble sodium bicarbonate, carbon dioxide, and a trace of sulfides. The temperature gradient in the carbonating towers is approximately 20 to 22°C at the bottom, 45 to 55°C in the center, and 25°C at the top. Lean carbon dioxide gases leaving the top of the carbonating towers and ammonia gas leaving the top of the absorber are led to the brine purification system for recovery.

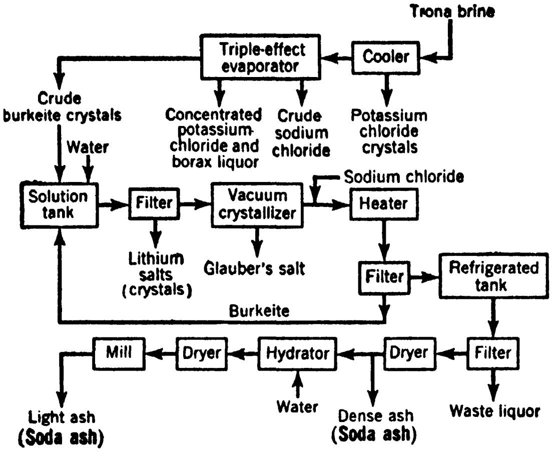
The bicarbonate slurry is filtered under vacuum, the filtered solid is conveyed to a calciner, the filtrate is sent to a free-ammonia still, and carbon dioxide and ammonia gases go back to the bottom of the carbonating tower.

Filter bicarbonate is heated to 175°C in a sealed rotary calciner, from which rich carbon dioxide gases are led to the second carbonating tower. The product, light ash (sp. gr. 0.55), goes to a cooler and thence to storage and packaging. Part of the dried product is added to the incoming wet bicarbonate to minimize caking in the dryer.

Dense ash (sp. gr. 1.0) may be made by adding a small amount of water to light ash in a mill, followed by dehydration in a second dryer or densifier, in which the dense ash crystals retain the shape of the monohydrate crystals.

Filtrate from the vacuum filter is pumped to a series of two ammonia stills: the first removes free ammonia; in the second still ammonium salts are decomposed by heating with milk of lime. Recovered ammonia is returned to the absorber with some make-up (usually 0.35 to 0.5 per cent of final soda). The effluent from the second still contains chiefly calcium chloride in solution, which may be sent to waste or to the calcium chloride-recovery plant.

From Lake Brines (Natural)



Reaction

$$Na_2CO_3 \cdot 2Na_2SO_4 \rightarrow Na_2CO_3 + 2Na_2SO_4$$

Material Requirements (Theoretical)

Basis—1 ton sodium carbonate (58%)

Saturated lake brine	43,000 lb

Process

Trona brine containing about 35 per cent solids (sp. gr. 1.3) is pumped through a series of condensers and filters to a triple-effect evaporator to effect a crude separation of the soluble salts into a potassium chloride–borax solution, solid crude sodium chloride, burkeite crystals ($Na_2CO_3 \cdot 2Na_2SO_4$) and solid dilithium sodium phosphate crystals (Li_2NaPO_4).

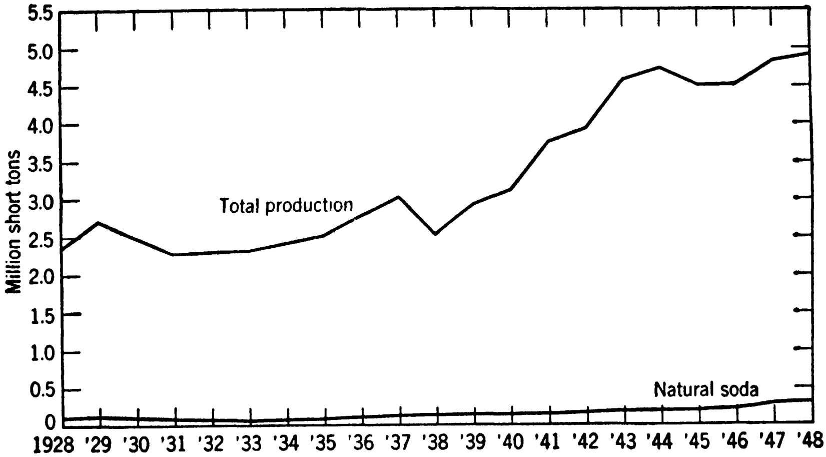
Soda ash is then produced from the burkeite crystals by the following process: The crystals are filtered from the evaporator slurry and redissolved in water. Dilithium sodium phosphate crystals do not dissolve and are filtered off. These crystals serve as a source of commercial lithium salts. The filtrate is heated to 28°C and concentrated in vacuum crystallizers to yield impure Glauber's salt ($Na_2SO_4 \cdot 10H_2O$). The Glauber's salt crystals are filtered off, leaving a mother liquor rich in sodium carbonate. Solid-salt crystals (NaCl) are dissolved in the mother liquor, and the mixture is heated to 53°C, at which temperature any remaining sodium sulfate crystallizes out as burkeite, which after filtration is returned to the main burkeite solution tank. The resulting filtrate is cooled to 5°C in a refrigerated tank where impure sal soda crystallizes. These crystals are filtered off and dried directly to dense ash. If light ash is desired, the dense ash is moistened with water, in a quantity that corresponds to the heptahydrate, and dried very slowly in a steam-heated dryer. After drying, the resulting material is ground to produce light ash.

In one of the more modern plants burkeite and the lithium salts from the evaporators are separated by flotation, before dissolving the burkeite crystals.

Recently, a lower salt body was discovered in Searles Lake, the brine from which is low in potash and high in sodium carbonate and sodium borate ($Na_2B_4O_7$). The brine is carbonated to allow sodium bicarbonate to precipitate and borax to remain in solution. After filtration, the bicarbonate is calcined to soda ash, and the filtrate is worked up for borax.

Electrolytic Soda Ash

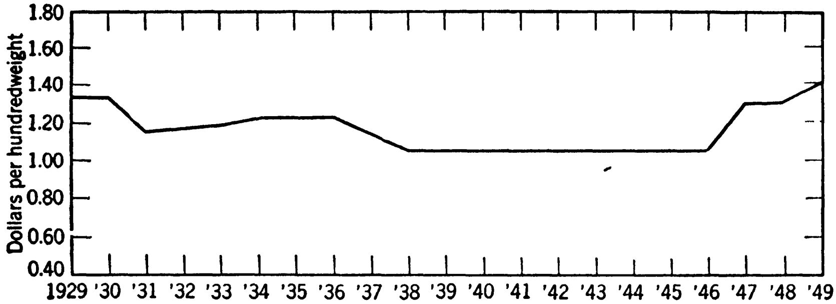
Electrolytic soda ash is produced by passing a current through a cell containing a saturated solution of salt in a manner similar to the chlorine-caustic process. See *Sodium Hydroxide.* At the cathode, however, carbon dioxide is bubbled into the solution and reacts with the sodium hydroxide formed. Sodium bicarbonate is precipitated, and then filtered, dried, and calcined to soda ash. See *Ammonia-Soda* process.



Production—Sodium Carbonate (Soda ash)

Use Pattern

	1948 (est.), per cent
Glass	28
Caustic soda and bicarbonate	23.5
Other chemicals	21.5
Pulp and paper	4.5
Nonferrous metals	4.0
Cleansers and modified sodas	2.5
Soap	3.0
Water softeners	2.0
Textiles	1.5
Petroleum refining	0.5
Miscellaneous and export	9.0
	100.0



Price—Sodium Carbonate (Soda ash)

Miscellaneous

Properties. White to grayish-white powder or lumps.

Mol. wt.	106.00	M.P.	851°C
Sp. gr.	2.533	B.P.	Decomposes

Soluble in water (7.1 g per 100 g at 0°C, 48.5 g per 100 g at 104°C). Insoluble in alcohol and ether.

Grades. Commercial, containing 82 per cent sodium carbonate (Na_2CO_3), 48 per cent sodium oxide (Na_2O); and 99 per cent sodium carbonate (58 per cent sodium oxide) in the following forms: light (48 and 58 per cent Na_2O), dense (48 and 58 per cent), 48 per cent ordinary (contains sodium chloride), 48 per cent special (contains sodium sulfate), granular, and extra light. The "light" and "dense" refer to apparent density, the dense preferred where small bulk is desired.

Containers and Regulations. Freight cars (bulk shipments), barrels, bags, and bottles. No ICC shipping label required.

Properties. *Sodium Carbonate Decahydrate,* sal soda, washing soda ($Na_2CO_3 \cdot 10H_2O$), white monoclinic crystals.

Mol. wt.	286.16	M.P.	32.5–34.5°C
Sp. gr.	1.46	B.P.	Loses H_2O at 33.5°C

Soluble in water (21.5 g per 100 g at 0°C, 238 g per 100 g at 30°C), insoluble in alcohol.

Grades. Technical.

Containers and Regulations. Same as soda ash.

Economic Aspects

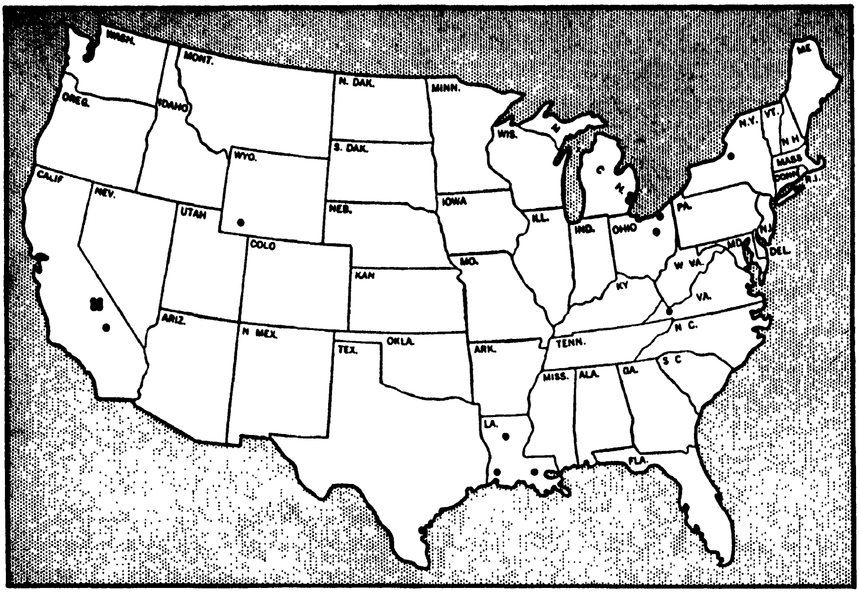
Soda-ash production, like that of sulfuric acid, is basic to American chemical production and a good indicator of general industrial status. The major production by far is by the ammonia–soda process, although some natural soda is produced from lake brines in California, and a very small amount is made electrolytically. In 1947 production percentages were 94 per cent, 6 per cent, and less than 1 per cent, respectively. Ammonia–soda plants are normally large with very few having a capacity smaller than 500 tons of soda ash daily. Plant-investment cost is in the neighborhood of $16,000 per ton daily capacity.

Most manufacturers also produce caustic, chlorine, and sodium bicarbonate. Because of the raw-material problem and disposal of by-products, many plants are tied in closely with coke-oven plants (by-product ammonia), the glass industry (largest single user of soda ash), the cement industry (to utilize lime sludge), and solid carbon dioxide manufacture (raw-material utilization).

Plants are delicately balanced, and stand-by equipment must be available to avoid shutdowns. Careful plant control is necessary to reduce ammonia (an expensive raw material) losses to a minimum, although with lower ammonia prices this factor is not so important as formerly.

Natural soda is only one of the many products derived from lake brines. Plants producing natural soda ash also produce borates, and many in addition produce potash, salt cake, lithium phosphate, or bromine. The largest such plant had a 1946 production of approximately 90,000 tons of soda ash, 200,000 tons of potash (as KCl), 100,000 tons of borax (including boric acid), and 140,000 tons of salt cake. Since then, soda-ash facilities have been expanded to approximately 150,000 tons. Operations were initiated in late 1947 to mine a trona deposit (96 per cent Na_2CO_3) near Green River, Wyo.

Soda ash is probably the most important alkali used in industry and competes with caustic soda, lime, and ammonia in this field. Low cost and high solubility make soda ash the most widely used of the group. In recent years ammonia has been offering more competition to soda ash as an alkali for general use.

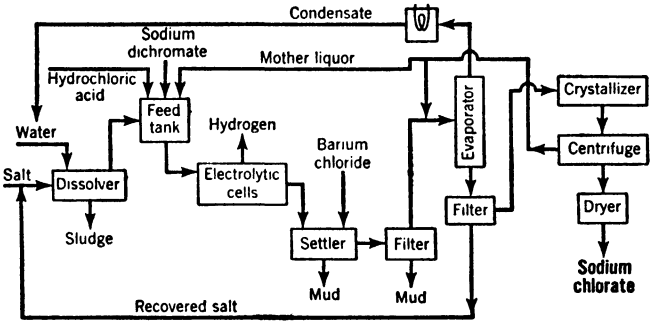


Location of Soda-Ash Plants

SODIUM CHLORATE

$NaClO_3$

From Salt by Electrolysis



Reaction

$$NaCl + 3H_2O + (6\,\text{Faradays}) \rightarrow NaClO_3 + 3H_2$$

95% yield
80% current efficiency

Material and Utility Requirements

Basis—1 ton sodium chlorate

Salt (sodium chloride)	1,130 lb	Barium chloride	13 lb
Hydrochloric acid (100%)	27 lb	Graphite consumed	20 lb
Sodium dichromate	10 lb	Electricity (a-c)	5,100 kw-hr

Process

Sodium chlorate is produced by the electrolysis of an acidified sodium chloride solution.

Salt (sodium chloride) is charged into a dissolving tank, where it is converted into a saturated solution by the addition of soft water. The condensate from the evaporator serves as a convenient source for the latter. Generally some mud and salt impurities collect at the bottom of the dissolver, from which they are periodically discharged. If the salt contains a high percentage of calcium and magnesium salts, it is usually necessary to purify the solution by precipitation, settling, and filtration of the foreign salts.

The clarified saturated salt solution is run into a feed tank, where it is mixed with dilute hydrochloric acid. A concentration of about 0.5 per cent acid is usually maintained so that the average *p*H of the brine solution in the cells will be approximately 6.5. Sodium dichromate (about 0.2 per cent) is added to inhibit cell corrosion caused by the liberated hypochlorous acid (from the hydrochloric acid present).

The saturated acidulated brine is fed into banks of electrolytic cells, operating batchwise or continuously, maintained at 40 to 45°C by cooling water. The construction and operation of the cells vary in different installations. Generally the cell bodies are constructed of steel (some are cement-lined) and make use of steel cathodes and graphite anodes. There is no diaphragm in the cell, and the electrodes are closely spaced to allow mixing of the products. The electrolysis actually yields chlorine at the anode and sodium hydroxide at the cathode. However, because of the foregoing conditions, good mixing occurs, resulting in the formation of sodium chlorate ($NaClO_3$) and sodium hypochlorite ($NaClO$). The latter is oxidized to the chlorate by the hypochlorous acid present. Hydrogen is liberated during the electrolysis and may be recovered by any suitable means.

The cells require d-c electric power, which is obtained by converting a-c power in mercury-arc or motor-generator rectifiers. For illustration, the approximate operating conditions of one plant are as follows:

Electric (a-c) power enters the plant at 34,500 volts and is stepped down by transformers to 4,800 volts. A motor-generator converts the alternating current to direct current and supplies power to long banks of series-connected cells at 250 volts. The cells are operated continuously by feeding a solution high in chloride ions and low in chlorate ions into the system, while an equal portion of liquor high in chlorate ions and low in chloride ions is simultaneously pumped out. The recirculated mother liquor (from the centrifuge) passes through a dissolver for sodium chloride fortification, prior to its reintroduction into the cell system. The cells are operated at 2,500 amperes per cell; the voltage drop per cell is 3.0 to 3.5. Current densities at the anode and cathode are 30 and 50 amperes per square foot, respectively. An average current efficiency of 75 per cent is obtained.

The cell liquors, after electrolysis, are discharged into a settler. In batchwise operation, generally 75 per cent of the salt is converted. The liquor in the settler may be heated to 90°C to destroy any residual hypochlorite. A small amount of barium chloride may be added to precipitate any chromate ions present. The graphite mud from the anodes and the barium chromate settle to the bottom of the tank and are periodically removed.

The liquor containing about 50 per cent sodium chlorate is decanted from the top of the settler, passed through a sand filter (if necessary), and charged into double-effect evaporators. Here it is concentrated to approximately 47°Bé (70 to 75 per cent sodium chlorate) and is filtered while hot. The unconverted sodium chloride is less soluble than the chlorate at boiling temperatures and is thrown out of solution. The recovered salt (filter cake) is returned to the dissolver for re-use.

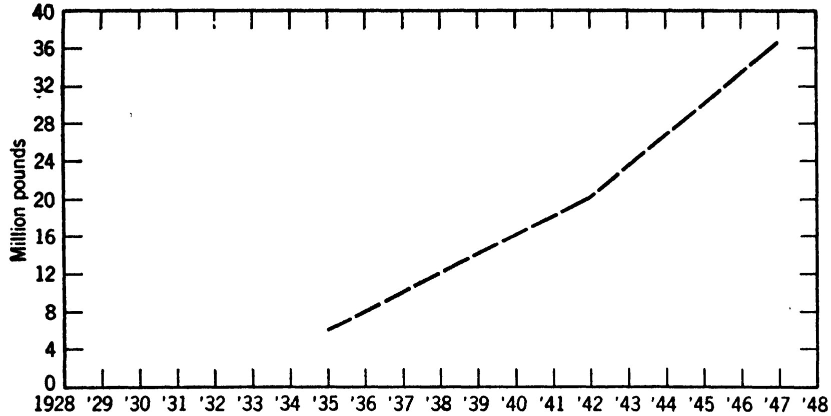
The filtrate is passed into a crystallizer, where it is cooled (below 30°C) to precipitate sodium chlorate crystals. The product is centrifuged, washed, and dried in rotary dryers. The centrifuge mother liquor and first wash liquors are generally returned to the evaporator for subsequent concentration, although periodically they are returned to the cell feed tank for reprocessing.

The dried product is ground to proper mesh size and screened to yield sodium chlorate crystals, which assay about 99.5 per cent. Although the initial conversion of sodium chloride to chlorate ranges from 50 to 75 per cent, the over-all yield (based on the salt charged) is about 95 per cent. The current efficiency averages 75 to 85 per cent, depending on the individual plant.

Sodium chlorate may be recovered from the cell liquors by other methods than the previously described concentration process. These other procedures include direct crystallization by refrigerative cooling (about 0°C) and salt exchange (isothermal crystallization) where the chlorate is salted out by addition of sodium chloride. See *Potassium Chlorate* for a description of the refrigeration method.

Sodium perchlorate ($NaClO_4$) is often manufactured in conjunction with sodium chlorate by the electrolysis of a saturated solution of the latter. The plant design is practically identical to the previously described chlorate plant. The reaction, $NaClO_3 + H_2O + (2\text{ Faradays}) \rightarrow NaClO_4 + H_2$) takes place in electrolytic cells equipped with platinum anodes and steel cathodes and operated at 65°C. Electrode current densities are 250 amperes per square foot at the anode and 140 amperes per square foot at the cathode. At 2,500 amperes per cell the voltage drop is 5.5 to 6.0 volts. The current efficiency averages 90 to 92 per cent.

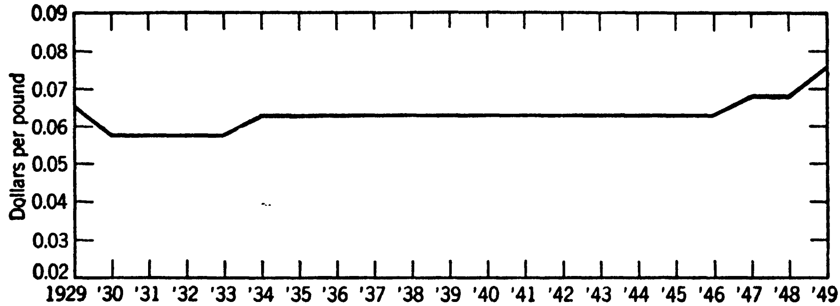
Perchlorate-recovery methods are similar to those used in chlorate plants. However, because of its extreme water solubility, sodium perchlorate is not generally isolated in crystalline form. Most of the material produced is further processed (in liquid form) to yield potassium perchlorate. See *Potassium Chlorate.*



Production—Sodium Chlorate (Estimated, except 1947)

Use Pattern

	Per cent
Herbicide	60
Miscellaneous, exclusive of wet crystals converted to perchlorates	40
	100



Price—Sodium Chlorate

Miscellaneous

Properties. Colorless, odorless cubic or trigonal crystals, with a cooling, saline taste.

Mol. wt.	106.45	M.P.	248°C
Sp. gr.	2.490 (15°C)	B.P.	Decomposes

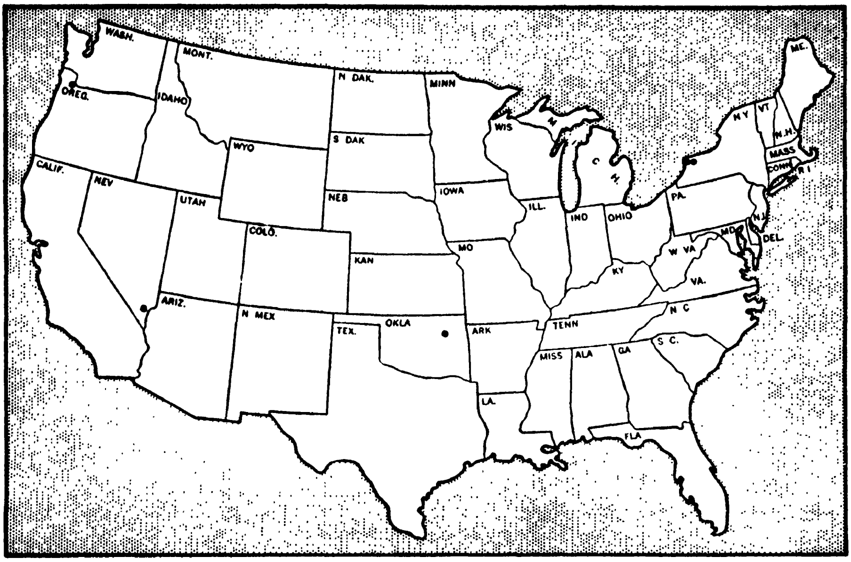
Soluble in water (79 g per 100 g at 0°C, 230 g per 100 g at 100°C), and alcohol.

Grades. Technical, C.P., and USP.

Containers and Regulations. Wooden kegs, steel drums, boxes, cartons, and bottles. Dangerous fire hazard in contact with combustible materials. Yellow ICC shipping label required.

Economic Aspects

The increase in sodium chlorate manufacture in recent years has been primarily caused by demand for a weed killer. Sodium chlorate solutions are certainly not the perfect weed killers and are considered by many agricultural authorities as the best of a not-too-good lot. Potential demand for a weed killer, particularly in the Great Plains States, is many times present consumption, but the cost of sodium chlorate delivered to the farmer is still considered too high for extensive use. This is true, in spite of the fact that dollar damage to crops by bindweed in the states mentioned runs into very large figures. Recent development of the hormone weed killers, such as 2,4-dichlorophenoxyacetic acid (see *2,4-D*), has also not solved the problem economically. It appears, then, that, until an effective, safe, and cheap weed killer appears on the market, use of sodium chlorate will remain in this field.



Location of Sodium Chlorate Plants

Of the two processes used for sodium chlorate production, the electrolytic process is by far the most important. Even in the chemical process, an electrochemical raw material, chlorine, must be used, so that production will continue to center around sources of cheap power. To afford economy of operation, any electrochemical process must be operated at a steady load throughout the year. For sodium chlorate, which is subject largely to seasonal demand, considerable warehouse space must therefore be provided. Accordingly, most manufacturers are engaged in the production of other electrochemical products, such as chlorine and caustic soda, so as to alleviate the effects of a seasonal product.

The chief variations in electrolytic processes for sodium chlorate are in recovery of the product from the cell liquors, which may be accomplished by chilling, salting out, or evaporation. The particular method used depends on conditions existing at a given plant. Considerable care must be taken in the operation of any chlorate plant, because of the potential fire and explosion hazard. A technical operating staff well versed in the control of operating hazards is accordingly a necessity in the industry.

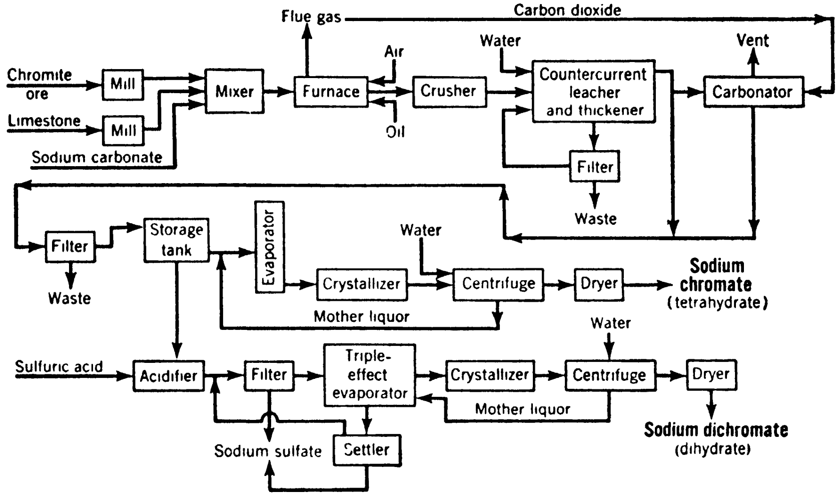
Commercial sodium chlorate plants are fairly large, with annual capacities usually in the range of 6,000,000 to 10,000,000 lb. Such plants require an investment of 10 to 15 cents per annual pound capacity. One plant design uses cells with a capacity of 625 lb sodium chlorate per cell per month. The early cells used platinum anodes, but these have since been superseded by cells using the cheaper graphite-impregnated anode.

SODIUM CHROMATE
SODIUM DICHROMATE

Na_2CrO_4

$Na_2Cr_2O_7$

From Chromite Ore



Reaction

$$4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$$

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + H_2O + Na_2SO_4$$

Material and Utility Requirements

Basis—1.6 ton sodium chromate decahydrate or
1 ton sodium dichromate dihydrate plus 0.5 ton sodium sulfate anhydrous

Chromite (50% Cr_2O_3)	2,200 lb	* Sulfuric acid (66°Bé)	1,000 lb
Limestone (calcium carbonate)	3,000 lb	Fuel oil	130 gal
Soda ash (sodium carbonate)	1,600 lb	Steam	6,000 lb
		Electricity	500 kw-hr

* Used in the production of dichromate only.

Process

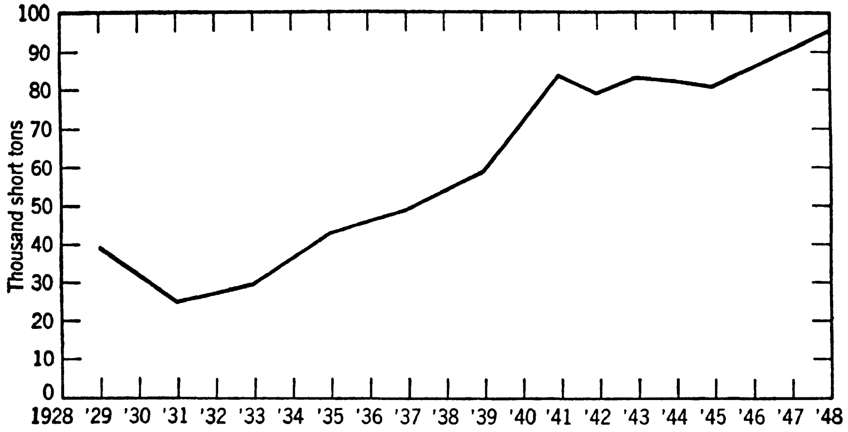
Sodium dichromate is produced by the reaction of sulfuric acid on sodium chromate, which in turn is obtained by calcining a mixture of chromite ore, limestone, and soda ash.

Chromite or chrome–ironstone is a chromium iron oxide ore containing principally ferrous chromite, $FeCr_2O_4$ or $(FeO \cdot Cr_2O_3)$, plus small amounts of aluminum, silicon, and magnesium oxides. High-grade chromite contains about 50 per cent chromium oxide (Cr_2O_3). This ore is imported principally from Southern Rhodesia, Union of South Africa, and New Caledonia. Low-grade ore (25 to 40 per cent Cr_2O_3) is mined domestically and occurs mainly in the northwest section of the United States. Most of the chromite ore used by the chemical industry is the imported high-grade variety.

Chromite is crushed and ground to a fine powder (150 to 200 mesh) in ball mills. It is charged into a mixer (rotary-bladed conveyer) with powdered (150- to 200-mesh) limestone (calcium carbonate) and soda ash (sodium carbonate). With an ore containing 50 per cent chromium oxide, a ratio of 2 parts chromite, 3 parts limestone, and 1.5 parts soda ash by weight may be used. The mixture is passed into a furnace or kiln, where it is calcined (roasted) at 850 to 1,070°C in a strongly oxidizing atmosphere. An oil- or gas-fired, mechanically rabbled reverberatory furnace with a single hearth is suitable for the calcination. With free exposure to air, the chromite reacts with the sodium carbonate and oxygen (in the air) to form sodium chromate while the iron is oxidized to ferric oxide. The principal function of the limestone is to increase the porosity of the charge and to reduce the agglomerating or fusion tendencies of the raw materials. It is also believed that the limestone acts as an oxidation promoter for the reaction. Practically complete conversion of chromite to soluble chromate is obtained; a small amount of insoluble calcium chromate is formed. Impurities in the original ore are generally oxidized. Carbon dioxide is liberated from both the limestone and soda ash.

At the end of the calcination (4 hr), the product is discharged from the furnace in the form of a semifused lump sinter. This calcine is crushed, ground to a powder, and classified. The material then is charged into countercurrent leaching tanks or thickeners (Dorr type), where the soluble chromate is dissolved in hot water and concentrated. The underflow from the last tray in the thickener, containing about 42 per cent insoluble matter, is filtered. The solids (principally insoluble iron oxide) are discharged to waste, and the mother liquor is returned to the leaching tank.

The overflow from the leacher, a clear solution containing about 35 per cent soluble chromate, is charged into either storage tanks or carbonators. The latter is used when prohibitive amounts of alkaline materials such as sodium aluminate and silicate are present. If a low-grade chromite ore serves as the raw material, these soluble impurities are carried along and tend to make the resulting solution more highly alkaline (*p*H about 10.5). The sodium silicate and sodium aluminate are precipitated by bubbling carbon dioxide through the chromate solution with mechanical agitation until a *p*H of about 8 is reached. The



Production—Sodium Chromate and Dichromate

*p*H of a corresponding solution of pure sodium chromate is 8.04. Flue gases from the furnace serve as a convenient source of carbon dioxide, and 3 to 4 cu ft of gas is sufficient to neutralize 1 gal of liquor. The neutralized solution is filtered to remove the precipitated impurities (discharged to waste) and is then run into storage tanks.

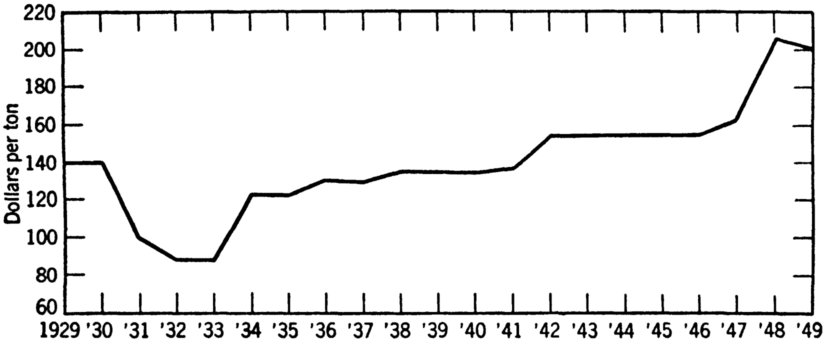
For sodium chromate production, the liquor from the tanks is concentrated in steel evaporators. The concentrate is discharged into a crystallizer where sodium chromate forms. The crystals are continuously centrifuged (the mother liquor is returned to the evaporators), washed, and dried in a rotary drum dryer. The yellow crystals of sodium chromate decahydrate are packaged for shipment.

For sodium dichromate production, the chromate solution from the storage tank is charged into an acidifier, where sulfuric acid is added until the *p*H of the liquor is reduced from 8.04 to 4.7. The chromate is converted to dichromate, with the resulting formation of sodium sulfate. Most of the latter crystallizes out of the boiling solution as anhydrous sodium sulfate. The crystals are removed by filtration, and the filtrate is charged into triple-effect evaporators, where the remainder of the sulfate crystallizes. The clear, hot, saturated dichromate solution (sp. gr. 1.7) is fed into a water-cooled crystallizer. Here, at about 20°C, approximately 70 per cent of the sodium dichromate crystallizes and is removed by continuous centrifuging. The mother liquor is returned to the evaporators. After drying in a rotary drum dryer, the red crystals of sodium dichromate dihydrate are packaged.

Both sodium chromate and dichromate may be purified by recrystallization from water.

Use Pattern

	Per cent
Pigments	45
Chemicals	15
Tanning	15
Metal treatment	8
Textiles	5
Miscellaneous and export	12
	100



Price—Sodium Dichromate

Miscellaneous

Properties. *Sodium Chromate* (Na_2CrO_4). Yellow, rhombic crystals.

Mol. wt.	162.00	M.P.	792°C
Sp. gr.	2.723		

Soluble in cold water and hot water (126 g per 100 g at 100°C).

Crystallizes from water as the decahydrate, $Na_2CrO_4 \cdot 10H_2O$, in the form of yellow deliquescent monoclinic crystals.

Mol. wt.	342.16	M.P.	19.9°C
Sp. gr.	1.483		

Very soluble in cold water; soluble in all proportions in hot water. Slightly soluble in alcohol.

Grades. Technical, pure neutral, highest purity, and C.P.

Containers and Regulations. Kegs, barrels, boxes, and bottles. No ICC shipping label required.

Properties. *Sodium Dichromate* ($Na_2Cr_2O_7 \cdot 2H_2O$). Bright orange deliquescent monoclinic crystals.

Mol. wt.	298.05	M.P.	Loses $2H_2O$ at 84.6°C
Sp. gr.	2.348 (25°C)		356.7 (anhydrous)°C
		B.P.	Decomposes at 400°C

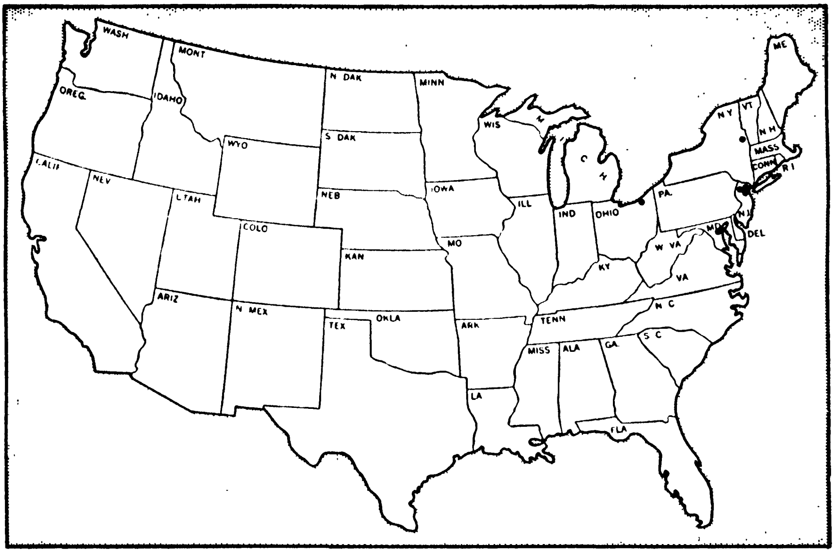
Soluble in water (70.6 per cent at 0°C, 88.4 per cent at 80°C).

Grades. Technical in crystal, granular, and anhydrous forms, and as 70% solution; C.P. crystals.

Containers and Regulations. Casks, barrels, kegs, drums, boxes, bags, cans, and bottles. No ICC shipping label required.

Economic Aspects

The manufacture of chrome chemicals is an old and specialized industry. Consequently, many plants, in the light of modern engineering knowledge, are obsolete, particularly with regard to high labor requirements and difficult working conditions. The preferred raw material is high-grade chromite from South Africa or the USSR. During the war a process was developed by the Bureau of Mines based on the use of low-



Location of Sodium Dichromate Plants

grade domestic ores. The prime product of the industry is sodium dichromate, which is then converted to other chromium-containing chemicals. The most modern plants use carbon dioxide instead of sulfuric acid to convert the chromate to dichromate, thus producing sodium bicarbonate as a by-product.

Most plants have a capacity of 5,000,000 to 15,000,000 lb of sodium dichromate per yr. It has been estimated that a 20-ton plant (14,000,000 lb per yr), utilizing the Bureau of Mines process, would cost $275,000.

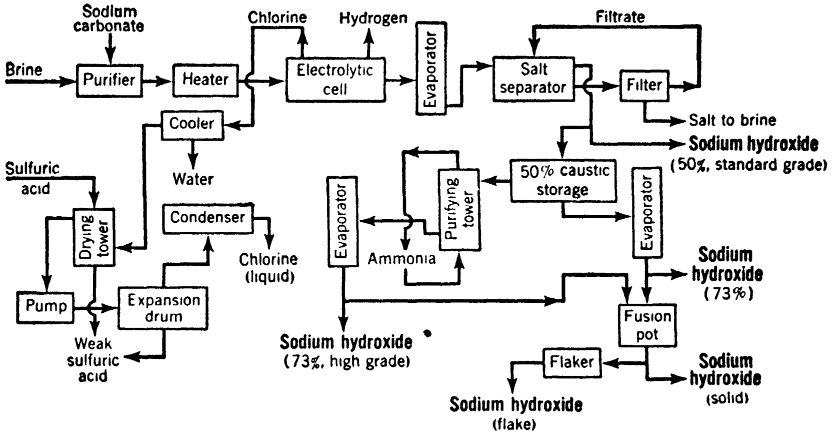
The major users of chrome chemicals are the leather-tanning and metal-treating industries. Trends in both industries indicate that even larger quantities may be required in the future.

SODIUM HYDROXIDE

(CAUSTIC SODA)

$NaOH$

From Salt by Electrolysis



Reaction

$$2NaCl + 2H_2O \xrightarrow[\text{current}]{\text{Direct}} 2NaOH + H_2 + Cl_2$$

95–97% current efficiency

Material and Utility Requirements

Basis—1 ton sodium hydroxide (99%)
plus 1,750 lb chlorine and 8,750 cu ft (50 lb) hydrogen

Salt	3,200 lb	Steam	20,000 lb
Sodium carbonate (58%)	50 lb	Electricity	2,500 kw-hr
Sulfuric acid (66°Bé)	200 lb	Refrigeration	1,800 lb

Process

In the electrolytic process for the manufacture of sodium hydroxide, an electric current is passed through a sodium chloride (salt) solution in specially designed cells. The salt brine is decomposed by the current to form a 10 to 12 per cent sodium hydroxide solution, with hydrogen gas forming at the cathode and chlorine gas at the anode as coproducts.

Salt, obtained from natural brines, mines, or the evaporation of sea water, is either dissolved in water or concentrated to produce a saturated solution of sodium chloride. The brine solution is heated and passed into purification tanks, where it is treated with sodium carbonate and some caustic soda to remove calcium and magnesium compounds. Barium chloride is often added if the brine has a high sulfate content. This purification procedure is necessary both to produce a high-grade product and also to reduce clogging of the diaphragm, if any, in the electrolytic cell. After the purified sodium chloride solution is neutralized with hydrochloric acid, the clear brine is reheated and fed to the cells for electrolysis.

Two general types of cells, the mercury cathode and diaphragm, are used in the United States. The mercury cell, of which the Castner cell is an example, is more expensive to operate because of the high initial investment in mercury (about 150 lb per cell) and because of the higher voltage required. In this cell, the mercury acts as the cathode, and metallic sodium released by the passage of the current amalgamates with the mercury. The amalgam is decomposed in another compartment of the cell by water to produce hydrogen and very pure (no chlorides) sodium hydroxide of 20 to 70 per cent concentration. Chlorine is formed at the graphite anodes, which operate at a current of about 630 amperes, with a voltage drop of 4.3 volts per cell. The current efficiency of these cells is about 95 per cent. The cells are operated at a temperature between 60 and 70°C.

The other general type of cell, the diaphragm cell, is exemplified by the Vorce cell (cylindrical) and Hooker S cell (rectangular). These cells contain a diaphragm of asbestos to separate the graphite anode from the steel screen or wire cathode. Brine flows into the anode compartment, where chlorine is formed, and then through the porous diaphragm, which allows the ions to pass but reduces diffusion of the products from the cathode compartment where sodium hydroxide and hydrogen are formed. Vorce cells and modified Vorce cells (double cathode) are operated with as many as 70 in series under a current of 1,000 to 1,600 amperes and 3.3 to 3.5 volts per cell (current efficiency, 94 to 97 per cent). The temperature is about 65°C. The Hooker S cell operates at a higher temperature (about 85°C) and current (7,500 amperes; average graphite anode life, 350 days; 96 per cent current efficiency), but usually at a lower voltage drop (about 3.4 to 3.5 volts per cell). It also has a larger capacity, resulting in more caustic and chlorine per cell. Other cells in use which resemble the Vorce cell are the Gibbs and Wheeler cells; the Nelson and Allen-Moore are of the rectangular type.

✓The diaphragm cell decomposes about 50 per cent of the brine to give 10 to 12 per cent caustic-soda solution, containing undecomposed sodium chloride. The weak caustic is charged to nickel-lined (to avoid iron contamination) multieffect evaporators, where 50 per cent sodium hydroxide solution is produced. Most of the salt precipitates out of the concentrated caustic and is recovered in salt separators. After filtering and washing, the salt is returned and used again to make up the charging brine. The 50 per cent caustic-soda liquor, which contains about 1 per cent sodium chloride, may be sold as is (standard-grade caustic liquor), or purified, or concentrated further.

Several purification processes may be used, and, depending on the procedure, either high-grade 50 per cent liquor or a high-quality concentrated product is obtained. Some of the troublesome impurities in 50 per cent caustic-soda solution produced by diaphragm-cell electrolysis are sodium chloride (about 2 per cent, dry basis), sodium chlorate (0.1 to 0.5 per cent, dry basis), and colloidal iron. The last is often removed by treating the liquor with 1 per cent by weight calcium carbonate and filtering the resulting mixture. The sodium chloride and chlorate may be removed by a countercurrent treatment of the liquor with 70 to 90 per cent ammonia in a liquid–liquid diffusion tower. The resulting 50 per cent high-grade caustic-soda liquor is as pure (virtually no chlorates and 0.1 to 0.2 per cent chloride, dry basis) as that produced in mercury cells, and it is either sold as such or concentrated.

Another method of reducing the salt content consists of cooling the liquor to 20°C and filtering off the crystallized sodium chloride. Other processes involve both purification and concentration. For example, ammonia may be added to the 50 per cent caustic-soda solution to precipitate sodium hydroxide monohydrate, which contains less water than the original liquor. Alternately, free-flowing anhydrous crystals of sodium hydroxide may be formed by treating the 50 per cent caustic with anhydrous ammonia in countercurrent pressure equipment.

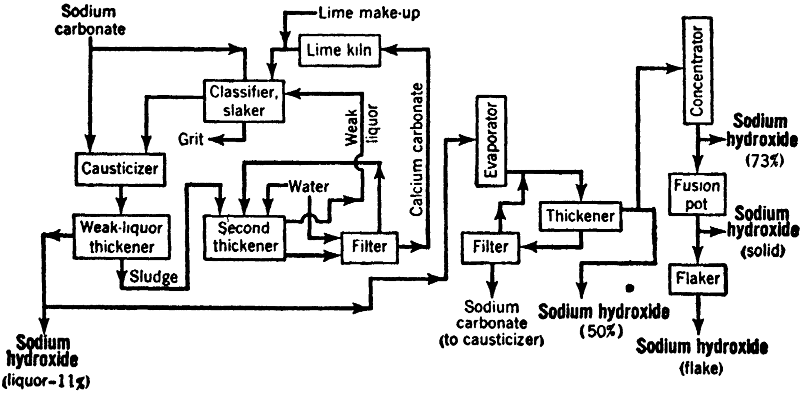
The 50 per cent standard-grade or high-grade caustic liquor may be run into single-effect evaporators, operating at 75 to 100 psi steam pressure to produce either 73 per cent standard- or high-grade caustic-soda liquor, depending on the purity of the dilute liquor used. These solutions (73 per cent) are handled in steam-jacketed pipes to prevent solidification (solidification point, 150°F) and are either charged into insulated tank cars equipped with steam coils or further dehydrated to yield solid sodium hydroxide.

The 70 to 75 per cent caustic-soda solution from the final evaporator is run to fusion pots constructed of special close-grained cast iron. Here at a final temperature of 500 to 600°C, essentially all the water (1 per cent or less) is boiled off. The molten caustic is generally treated with sulfur to precipitate iron, and after settling it is discharged into thin steel drums for sale as solid caustic, or the hot anhydrous sodium hydroxide is run to a flaker to produce flaked caustic. Depending on the purity of the 73 per cent caustic liquor charged, governed by purification or manufacturing processes, either standard-grade anhydrous caustic soda, containing 2 to 3 per cent impurities, or high-grade sodium hydroxide (anhydrous) with less than 1 per cent impurities is obtained. In addition to the liquid, solid, and flake forms, caustic soda is also produced in ground and powdered grades, obtained by breaking or pulverizing the solid form.

The hot, wet chlorine gas, which is evolved at the anodes of the cells, is recovered after cooling, to condense most of the water, and dried in a sulfuric-acid scrubber. The gas is then compressed and cooled to form liquid chlorine, which is stored or filled into cylinders for sale. Details on the production of chlorine by electrolysis of salt are given under *Chlorine.*

Hydrogen, produced at the cell cathode, is dried and compressed by methods shown under the heading, *Hydrogen.*

From Lime and Soda Ash



Reaction

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + CaCO_3$$

88–90% yield

Material and Utility Requirements

Basis—1 ton sodium hydroxide (in 11% solution)

Sodium carbonate (58%)	3,000 lb	Steam	2,700 lb
Lime (make-up—90% CaO)	165 lb	Fuel (reburning)	13,000,000 Btu
Water	2,200 gal	Electricity	18 kw-hr

Process

In the lime–soda process, a solution of sodium carbonate (soda ash) is treated with calcium hydroxide (slaked lime) to produce a precipitate of calcium carbonate and an aqueous solution of sodium hydroxide. After removal of the insoluble carbonate, the solution is concentrated to give various grades of caustic soda for sale.

The process may be operated on a batchwise or a continuous basis. In the latter, a 20 per cent solution of sodium carbonate is charged into a causticizer with a slight excess of slaked or milk of lime. The reaction is carried out at about 85°C.

After agitating for about 1 hr, the solution is settled in thickeners. These are usually of the multitray design (Dorr type) and consist of two or three units in series. The overflow solution from the first or weak-liquor thickener is run to the evaporators for concentration or is used as a finished product. The solution contains 10 to 12 per cent sodium hydroxide and is obtained at a conversion of 95 to 96 per cent based on sodium carbonate.

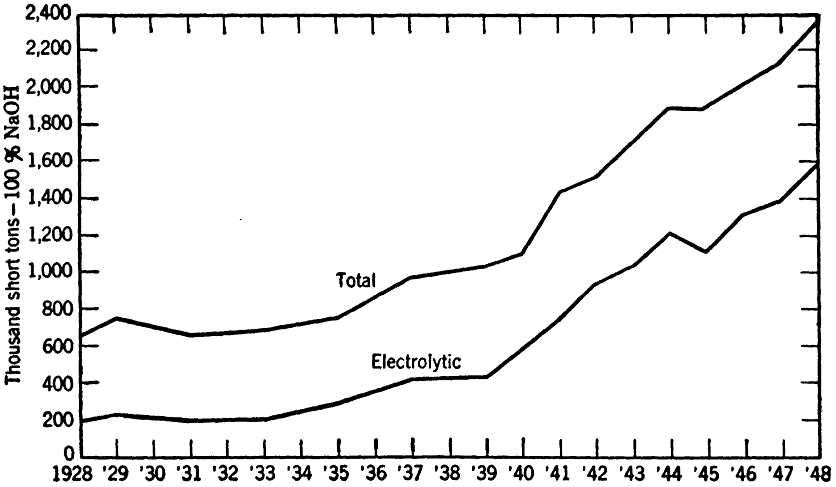
The sludge from the bottom of the first thickener is pumped to a second thickener, where hot water and the filtrate from the subsequent operation are added. The liquor overflowing from this thickener contains sodium hydroxide and carbonate in weak concentrations and is generally used as weak liquor to make up the original 20 per cent sodium carbonate (soda-ash) solution. The sludge from the second thickener is filtered (Oliver filter) and washed. The filtrate is returned to the second thickener as mentioned, whereas the filter cake, which consists mostly of calcium carbonate, is sent to a lime kiln to furnish reburned lime (calcium oxide). This material is fed along with the soda-ash solution to a combination classifier–slaker, where milk of lime is formed and the grit removed to give the slurry, which is fed to the causticizers to start the process.

The clear liquor from the first thickener contains about 11 per cent sodium hydroxide and 1.7 per cent sodium carbonate. This weak solution is concentrated in multiple-effect evaporators to produce 50 per cent sodium hydroxide. As the concentration of sodium hydroxide increases, the sodium carbonate becomes less soluble and is finally precipitated so that the finished 50 per cent caustic-soda solution contains only about 0.15 per cent sodium carbonate. After settling in another thickener, the clear solution is stored. The sludge from the bottom of the thickener is filtered on an Oliver filter; the filtrate is returned to the thickener.

The filter cake, consisting mostly of unreacted sodium carbonate and whatever sodium chloride was present in the original soda ash, is returned to the causticizer.

The 50 per cent sodium hydroxide solution is either sold from storage or concentrated further, as described in the previous section on electrolytic caustic soda.

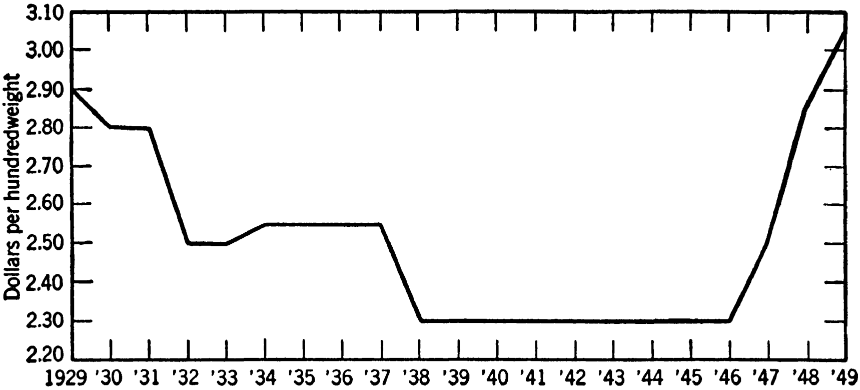
Instead of the usual fusion process for removal of water, anhydrous caustic soda may be obtained by a partial pressure procedure. Kerosene or some other hydrocarbon is fed with the concentrated caustic solution into an evaporator, where it is distilled out along with the water. The water is removed at a much lower temperature, which decreases the heat requirements in addition to producing a crystalline product on a continuous basis. In some recent plants solid caustic soda is produced from 50 per cent liquor continuously in a single-pass evaporator heated with Dowtherm.



Production—Sodium Hydroxide (Caustic soda)

Use Pattern

	1948 (est.), per cent
Chemicals	22.0
Rayon and film	22.0
Petroleum refining	7.7
Pulp and paper	6.3
Lye and cleansers	5.8
Soap	5.2
Textiles	5.0
Rubber reclaiming	1.3
Vegetable oils	1.0
Miscellaneous and export	23.7
	100.0



Price—Caustic Soda

Miscellaneous

Properties. White, deliquescent pieces, lumps, or sticks. Absorbs both carbon dioxide and water from the air.

Mol. wt.	40.00	M.P.	318.4°C
Sp. gr.	2.130	B.P.	1,390°C

Soluble in water (42 g per 100 g at 0°C, 347 g per 100 g at 100°C), alcohol, ether, and glycerine. Insoluble in acetone.

Grades. USP, C.P., reagent, and commercial in the form of flakes, granulated, ground, sticks, lumps, and drops (pellets). The common grades based on sodium oxide (Na_2O) content are 60 per cent (77.4 per cent sodium hydroxide, $NaOH$), 70 per cent (90.3 per cent sodium hydroxide), 74 per cent (95.48 per cent sodium hydroxide), and 76 per cent (98.06 per cent sodium hydroxide). Aqueous solutions (containing about 50 per cent and 73 per cent sodium hydroxide) are available and weigh about 12.5 lb per gallon.

Containers and Regulations. Solid: drums, barrels, cans, and bottles. No ICC shipping label required. Liquid: insulated tank cars, drums, and barrels. White ICC shipping label required.

Economic Aspects

The manufacture of caustic soda is related both to the chlorine industry and to the ammonia–soda industry in that it is produced as a profitable item by both. In the first case, caustic soda is a joint product with chlorine; in the second, production is secondary to soda ash, albeit competitive and profitable. During the early part of the present century, chemical caustic, manufactured primarily by ammonia–soda producers, far outshadowed electrolytic caustic, but in the late 1930's production of the latter passed the production of chemical caustic and has remained in the lead ever since. The percentage of total production manufactured by the electrolytic process was 29 per cent in 1925, 44 per cent in 1935, and nearly 70 per cent in 1948. How far this trend may go is a matter of conjecture. The final answer, of course, is the cost of caustic delivered to the customer in the form in which he wants it. However, demand for chlorine is increasing faster than demand for caustic soda, and ultimately this condition can only be detrimental to production of chemical caustic. There is a definite tendency for chlorine consumers to build electrolytic plants to supply their own chlorine needs and to market excess caustic. Such practice could ultimately lead to much lower caustic prices, not only forcing ammonia–soda producers out of the caustic-soda business, but also taking away a portion of their soda-ash business.

On the other hand, companies needing large quantities of caustic soda and little chlorine can often build their own causticizing plants, and consume the product in solution as manufactured. Many soap manufacturers follow this practice.

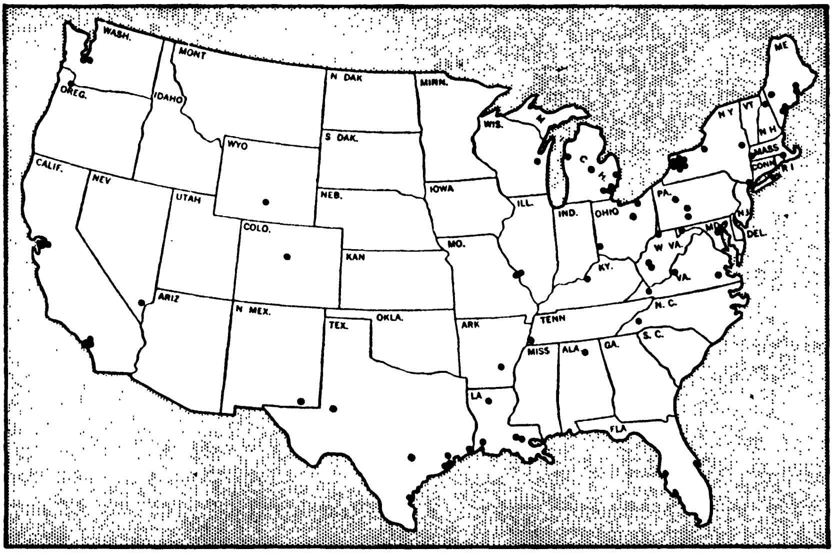
Within the electrolytic chlorine–caustic industry, primary competition centers around cell design and power costs. The general trend is toward larger cells with high capacity per square foot of floor space (see *Chlorine*). One of the most important current problems of the industry is production of caustic soda sufficiently pure for use in its largest single market: rayon manufacture. Diaphragm cells produce 12 per cent caustic-soda solution, containing both sodium chloride (2 per cent, dry basis) and sodium chlorate (0.1 to 0.5 per cent, dry basis). Several purification processes are used, but the most promising is the recent ammonia-treatment process, by means of which impurities can be reduced to 0.0 per cent chlorate and 0.1 to 0.2 per cent chloride (dry basis). Considerable interest is being shown in a German mercury cell discovered by

Allied technical teams studying German industry. This cell produces directly 50 to 70 per cent caustic-soda solution of rayon grade and is said to show economic promise. A similar American cell has also been developed. The status of mercury-cell design is still uncertain. Three recent installations each have used a different cell.

For years, shipment of caustic soda has also been a troublesome problem, which has led many consumers to building their own caustic units. Recent development of an insulated tank car with a modified ethyl cellulose lining allows shipment of 70 to 74 per cent caustic-soda solutions without contamination and may reverse the trend to construction of consumer caustic plants.

Cost and sizes of electrolytic plants are discussed under *Chlorine*. A small lime–soda plant is one with a capacity of 15 to 20 tons of caustic soda per day. Large continuous plants vary in size from 50 to 500 tons of caustic soda per day. Most of the caustic soda from these plants is used or sold as 50 per cent caustic liquor, and more recently as 70 and 74 per cent liquors. The size of plants making solid or flake caustic soda depends on fusion-pot size. The pots usually have capacities of 12 to 18 tons of caustic soda per batch. The pot cycle varies from 4 to 6 days.

The by-product of the lime–soda process is "caustic sludge" (alkaline calcium carbonate), which is returned to a lime kiln or a cement plant, converted to whiting, or wasted.

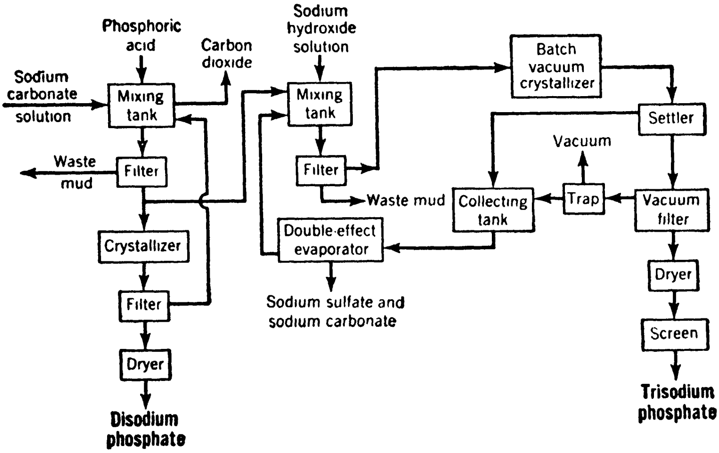


Location of Caustic-Soda Plants

SODIUM PHOSPHATE

Monobasic	NaH_2PO_4
Dibasic	Na_2HPO_4
Tribasic	Na_3PO_4
Tetrabasic	$Na_4P_2O_7$
Acid	$Na_2H_2P_2O_7$
Meta	$(NaPO_3)_6$

From Phosphoric Acid and Sodium Carbonate



Reaction

$$Na_2CO_3 + H_3PO_4 \rightarrow Na_2HPO_4 + CO_2 + H_2O$$

$$Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O$$

90–95% yield

Material Requirements

Basis—1 ton trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$)

Phosphoric acid (45% P_2O_5)	880 lb
Sodium carbonate (58% Na_2O)	600 lb
Sodium hydroxide (76% Na_2O)	240 lb

Process

Sodium phosphates are produced by processing the reaction products of phosphoric acid and soda alkalies. Since phosphoric acid (orthophosphoric acid) is a tribasic acid, it forms three sodium salts. Sodium meta- and pyrophosphates are obtained by heating the corresponding sodium orthophosphate.

Disodium phosphate, Na_2HPO_4, is known as ordinary "sodium phosphate" of commerce and may be considered the base of all the other phosphates. It is produced as an intermediate in the manufacture of trisodium phosphate (Na_3PO_4), which is the most important phosphate as far as quantity produced is concerned. Description of the manufacture of disodium phosphate and trisodium phosphate follows:

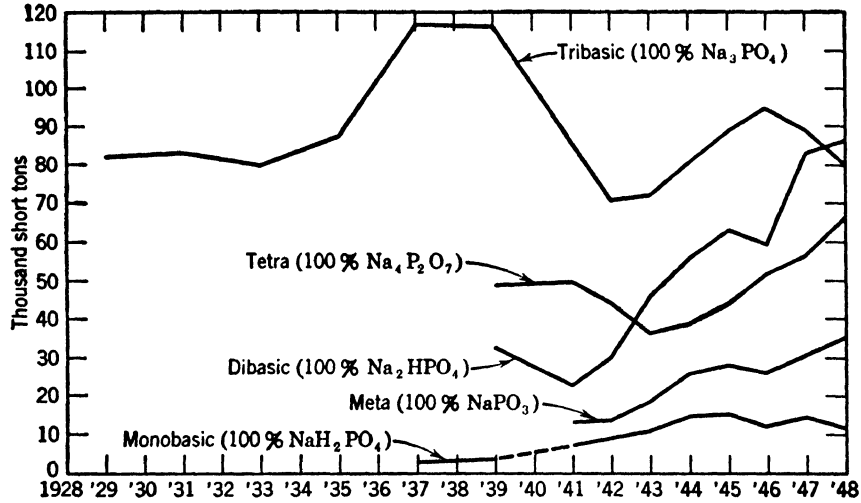
Sodium carbonate (soda ash) is introduced into a mixing tank, either as an aqueous solution or as a solution made with hot liquor from the evaporators or mother liquor from the filters. Phosphoric acid (60 to 65 per cent H_3PO_4) is added at the surface of the tank so that carbon dioxide can be liberated easily. A slight excess of sodium carbonate over the theoretical ratio is added, and the solution is boiled with steam until all the carbon dioxide has been driven off. The resulting disodium phosphate solution is filtered hot (85 to 100°C) and is split into two portions. A small amount of white mud, consisting of silica and iron and aluminum phosphates, remains on the filter and is discharged to waste. Part of the clear solution of disodium phosphate, containing about 14.5 per cent phosphorus pentoxide and 13 per cent sodium oxide, is pumped to a trisodium phosphate process tank.

The remainder of the solution is cooled in a crystallizer to yield crystals of disodium phosphate, containing 12 molecules of water of crystallization (60 per cent water). These crystals, $Na_2HPO_4 \cdot 12H_2O$, are centrifuged and packaged in moisture-proof containers. The mother liquor is returned to the mixing tank. The crystals are efflorescent, losing 5 molecules of water and forming the heptahydrate ($Na_2HPO_4 \cdot 7H_2O$) on exposure to air. The crystals may be dried to yield the dihydrate ($Na_2HPO_4 \cdot 2H_2O$, containing 20 per cent water) or the anhydrous salt (Na_2HPO_4).

To the hot disodium phosphate solution in the trisodium phosphate process tank is added 50 per cent sodium hydroxide (caustic-soda) solution. The solution is maintained at about 90°C, and control samples are taken and titrated to control the operation. The hot solution is filtered (on a rotating leaf pressure filter) to remove any insolubles (white mud) and is passed into batch-type vacuum crystallizers. Crystals of trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$) form and are allowed to separate in a settler. The clear liquor and mother liquor from the filter are collected and condensed in a double-effect evaporator. Sodium sulfate and sodium carbonate are discharged from the bottom of the evaporator while the concentrated liquor is returned to one of the mixing tanks for reprocessing.

The settled crystals of trisodium phosphate are separated from the remaining mother liquor on rotary vacuum filters. The crystals are further dried in rotary dryers (below 70°C), screened, and packaged. By drying above 100°C, the hydrate loses 11 molecules of water to yield trisodium phosphate monohydrate ($Na_3PO_4 \cdot H_2O$). Trisodium phosphate ($Na_3PO_4 \cdot 12H_2O$) is obtained in a 90 to 95 per cent yield based on the weight of phosphoric acid charged.

Monosodium phosphate is produced by adding the requisite amount of phosphoric acid to a concentrated solution of disodium phosphate.



Production—Sodium Phosphate

The resulting solution, on evaporation, yields crystals of monosodium phosphate monohydrate ($NaH_2PO_4 \cdot H_2O$). The anhydrous salt (NaH_2PO_4) may be produced by desiccating the hydrate at normal temperatures.

By heating the phosphate between 225 and 250°C for 6 to 12 hr, the reaction ($2NaH_2PO_4 \rightarrow Na_2H_2P_2O_7 + H_2O$) takes place, yielding the nonhygroscopic salt, sodium-acid pyrophosphate. This salt is more stable than the monosodium phosphate and is used generally for the same purposes (baking-powder formulations).

On heating monosodium phosphate to 350 to 400°C, an insoluble metaphosphate is formed. If the monosodium salt is fused to approximately 760°C and quickly cooled [$6NaH_2PO_4 \rightarrow (NaPO_3)_6 + 6H_2O$], sodium hexametaphosphate results.

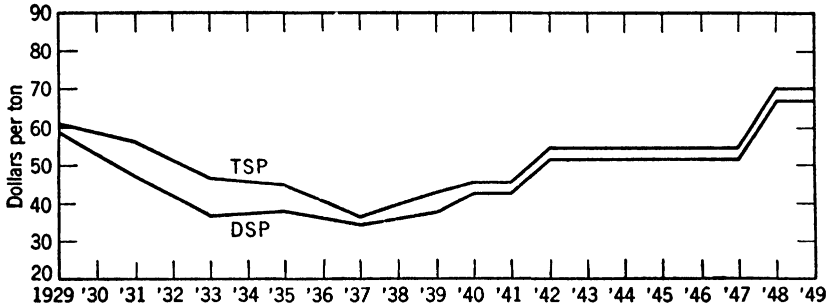
Tetrasodium pyrophosphate, $Na_4P_2O_7$, is manufactured by dehydrating disodium phosphate in a rotary kiln according to the reaction: $2Na_2HPO_4 \rightarrow Na_4P_2O_7 + H_2O$. Both the anhydrous salt ($Na_4P_2O_7$) and the crystalline decahydrate ($Na_4P_2O_7 \cdot 10H_2O$) are produced, depending on the operating conditions.

Various phosphate salts known as polyphosphates may be produced from mixtures of mono- and disodium phosphates. These materials, in general, are of rather indefinite molecular composition. Sodium tripolyphosphate, $Na_5P_3O_{10}$, is the only definitely crystalline polyphosphate and is produced by slowly cooling the proper proportions of mono- and disodium phosphate previously heated between 300 and 500°C.

Practically all the afore-mentioned sodium phosphates are produced commercially in more than one form. Usually they are obtained as the above-described hydrates. However, other hydrates are known and may be produced by varying the crystallization and drying operations.

Use Pattern

(All sodium phosphates)	Per cent
Various detergent uses	50
Water conditioning	20
Food and medicine	10
Miscellaneous	20
	100



Price—Sodium Phosphate

Miscellaneous

Monosodium Phosphate. Sodium phosphate monobasic, sodium acid phosphate, sodium bisphosphate, sodium dihydrogen phosphate, or monosodium orthophosphate.

Properties. Monohydrate: $NaH_2PO_4 \cdot H_2O$, large, transparent, colorless, rhombic crystals which are acid in reaction.

Mol. wt.	138.01	M.P.	Loses H_2O at 100°C
Sp. gr.	2.040	B.P.	Loses $2H_2O$ at 200°C, decomposes

Soluble in water (71 g per 100 g at 0°C, 390 g per 100 g at 83°C, 427 g per 100 g at 100°C). Insoluble in alcohol.

Grades. Commercial and food.

Containers and Regulations. Barrels, bags, kegs, and bottles. No ICC shipping label required.

Disodium Phosphate. DSP, sodium phosphate dibasic, secondary sodium phosphate, sodium hydrogen phosphate, phosphate of soda, sodium phosphate or disodium orthophosphate.

Properties. Crystalline: $Na_2HPO_4 \cdot 12H_2O$—colorless, translucent, monoclinic crystals.

Mol. wt.	358.17	M.P.	34.6°C
Sp. gr.	1.52	B.P.	Loses 12 H_2O at 180°C

Soluble in water (4.3 g per 100 g at 0°C, 76.7 g per 100 g at 30°C). Insoluble in alcohol.

Dihydrate: $Na_2HPO_4 \cdot 2H_2O$—colorless crystals.

Mol. wt.	178.05	M.P.	Loses H_2O at 92.5°C
Sp. gr.	2.066 (15°C)		

Soluble in water (82.5 g per 100 g at 50°C, 96.6 g per 100 g at 80°C.

Grades. Commercial, food, and USP medicinal.

Containers and Regulations. Barrels, bags, kegs, boxes, and bottles. No ICC shipping label required.

Trisodium Phosphate. TSP, sodium phosphate tribasic, normal sodium phosphate, tertiary sodium phosphate, or trisodium orthophosphate.

Properties. Crystalline: $Na_3PO_4 \cdot 12H_2O$—colorless or white trigonal crystals.

Mol. wt.	380.16	M.P.	73.4°C, with decomposition
Sp. gr.	1.62 (20°C)	B.P.	Loses $11H_2O$ at 100°C

Soluble in water (28.3 g per 100 g at 15°C, in all proportions in hot water). Insoluble in carbon disulfide.

Grades. Commercial, C.P., and highest purity in various mesh sizes (coarse, regular, medium, fines, and powder).

Containers and Regulations. Barrels, bags, kegs, boxes, fiber drums, and bottles. No ICC shipping label required.

Tetrasodium Pyrophosphate. TSPP, sodium phosphate tetrabasic, sodium tetraphosphate, sodium pyrophosphate, pyrophosphate of soda, normal pyrosodium phosphate, or alkaline sodium pyrophosphate.

Properties. Crystalline: $Na_4P_2O_7 \cdot 10H_2O$—colorless monoclinic crystals.

Mol. wt.	446.11	M.P.	940°C
Sp. gr.	1.82		

Soluble in water (5.4 g per 100 g at 0°C, 93 g per 100 g at 100°C). Insoluble in alcohol and ammonia.

Anhydrous: $Na_4P_2O_7$—white crystals.

Mol. wt.	265.95	M.P.	988°C
Sp. gr.	2.45		

Soluble in water (3.2 g per 100 g at 0°C, 40.3 g per 100 g at 100°C). Decomposes in alcohol.

Grades. Crystalline and anhydrous.

Containers and Regulations. Barrels, bags, kegs, and bottles. No ICC shipping label required.

Sodium Acid Pyrophosphate. Disodium dihydrogen pyrophosphate, disodium pyrophosphate, acid sodium pyrophosphate.

Properties. Anhydrous: $Na_2H_2P_2O_7$—white powder.

Mol. wt.	221.97	M.P.	Decomposes 220°C
Sp. gr.	1.862	B.P.	—

Soluble in water.

Grades. Commercial and food.

Containers and Regulations. Barrels, bags, kegs, and bottles. No ICC shipping label required.

Sodium Metaphosphate. Sodium hexametaphosphate, Graham's salt.

Properties. $(NaPO_3)_6$—colorless or white flakes.

Mol. wt.	612.10	M.P.	640°C
Sp. gr.	2.181	B.P.	Sublimes > 1,000°C

Soluble in hot and cold water.

Grades. Commercial.

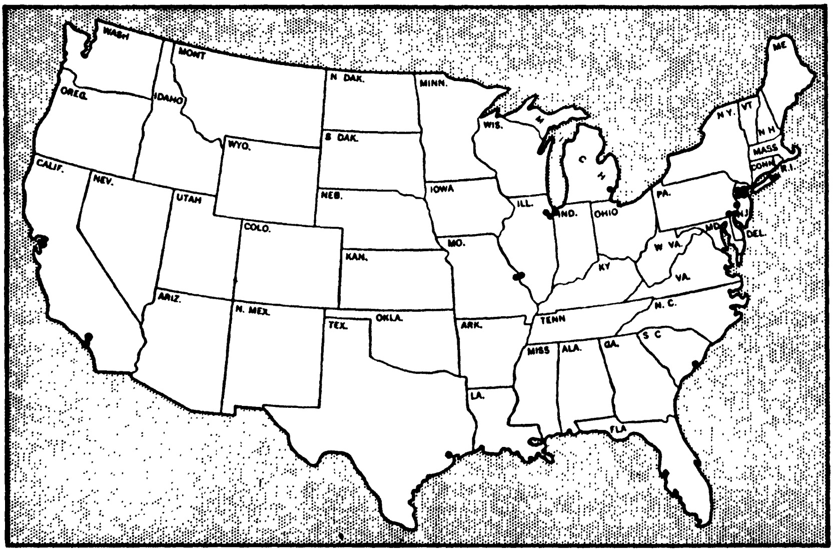
Containers and Regulations. Barrels, bags, kegs, and bottles. No ICC shipping label required.

Economic Aspects

Trisodium phosphate (TSP) is the most important single compound of the various sodium phosphates (mono-, di-, tri-, meta-, and tetrasodium pyrophosphate). Most of its uses center around the property of forming well-buffered highly alkaline solutions in water. For many of its uses, particularly in the field of water conditioning, it is being replaced by the metaphosphates which, although more expensive, are much more effective in suppressing calcium ions. Disodium phosphate replaces trisodium phosphate for some uses where lower alkalinities are desired. Monosodium phosphate is used principally in the formulation of baking powders but is secondary to monocalcium phosphate for this use. In either case some competition exists with cream of tartar and soda alum. Tetrasodium pyrophosphate is largely used as a "builder" in various cleaners and cleansers.

The three basic sodium phosphates are derived from phosphoric acid at present, although numerous attempts are being made to use phosphorus-containing minerals, such as apatite, for trisodium phosphate manufacture. The natural manufacturers, of course, of the sodium phosphates are those also producing phosphoric acid or manufacturing a general line of heavy chemicals.

The processes used are essentially batch in character and accordingly vary greatly in size.

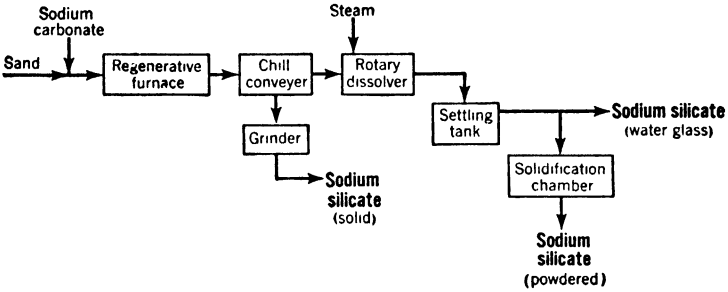


Location of Sodium Phosphate Plants

SODIUM SILICATE

Sodium tetrasilicate (water glass)	$Na_2Si_4O_9$
Sodium metasilicate	Na_2SiO_3
Sodium sesquisilicate	$Na_3HSiO_4 \cdot 5H_2O$
Sodium orthosilicate	Na_4SiO_4

From Sodium Carbonate and Silica (Sand)



Reaction

$$Na_2CO_3 + SiO_2 \rightarrow \underset{\substack{(Na_2SiO_3)\\ \text{Sodium metasilicate}}}{Na_2O \cdot SiO_2} + CO_2$$

Material and Utility Requirements

Basis—1 ton 40°Bé sodium silicate (water glass)

Sodium carbonate (dense, 58%)	312 lb	Water	160 gal
Sand	586 lb	Steam	1,040 lb
Gas (1,000 Btu)	5,000 cu ft	Electricity	21.6 kw-hr

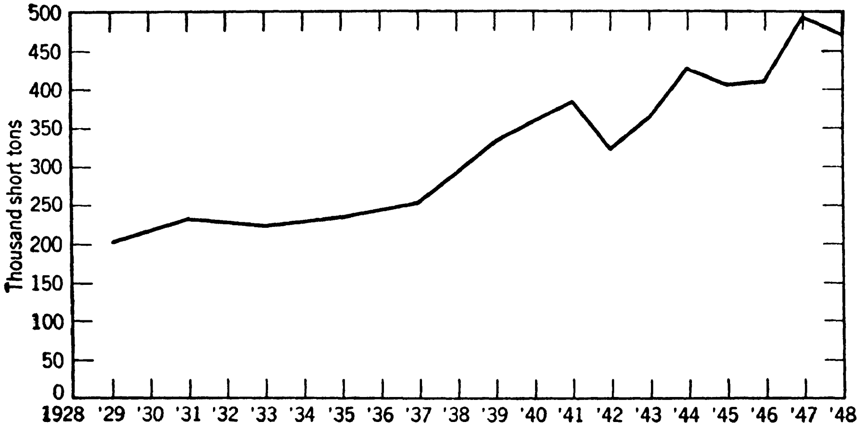
Process

A variety of compounds, ranging in chemical composition from $Na_2O \cdot 4SiO_2$ to $2Na_2O \cdot SiO_2$, is produced by the fusion of silica (sand) and sodium carbonate (soda ash). By properly proportioning the reactants, the ratio of the constituent parts (Na_2O and SiO_2) may be varied to obtain a number of desired properties. Sodium silicates, varying in ratio from $Na_2O \cdot 1.6SiO_2$ to $Na_2O \cdot 4SiO_2$, are known as colloidal silicates.

These are generally sold as 20 to 50 per cent aqueous solutions called water glass. They are so named because they solidify to a glass which is water-soluble.

Sodium metasilicate (Na_2SiO_3) has the ratio of $Na_2O \cdot SiO_2$ and is a definite crystalline compound, which forms various hydrates. Substances having higher sodium oxide content are sodium sesquisilicate ($1.5Na_2O \cdot SiO_2$) and sodium orthosilicate, Na_4SiO_4, ($2Na_2O \cdot SiO_2$).

The more siliceous sodium silicates are glasses, typical noncrystalline solid solutions, which are important mostly for their adhesive and binding properties. The more alkaline silicates (including sodium metasilicate) are crystalline materials with definite structures and characteristic properties. These are used chiefly as cleaners and detergents.



Production—Sodium Silicate (Anhydrous basis—liquid and solid)

Sand and sodium carbonate, in selected proportions, are charged batchwise into a regenerative tank furnace resembling that used for the manufacture of glass. Fuel gas (producer, coke-oven, or natural) and air are mixed, preheated, and burned to maintain oven temperatures of 2,200 to 2,600°F in the hot zone. The melted materials gradually flow through the furnace evolving carbon dioxide. There is a normal shrinkage (approximately 10 per cent) in the weight of the charge, due to the loss of gases and volatilization of alkali oxides.

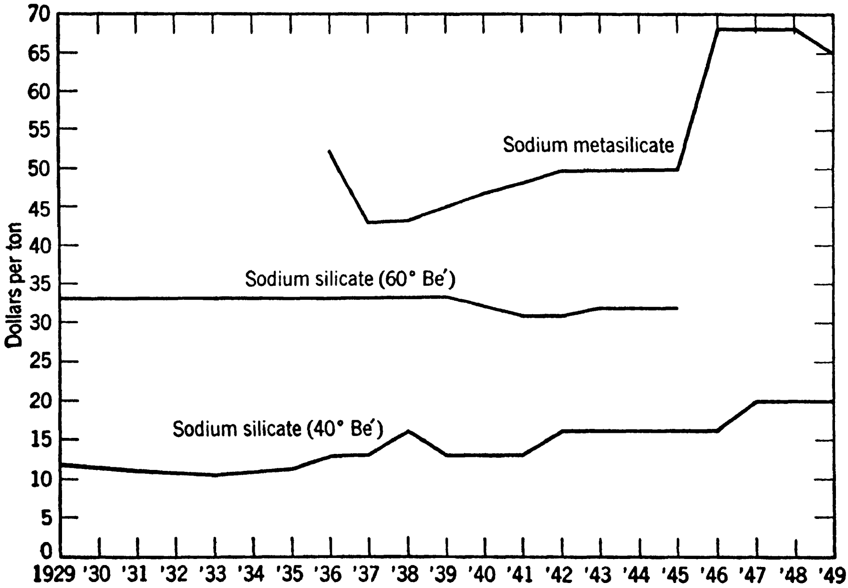
The fused melt is drawn from the furnace continuously or periodically as a thin stream. This is solidified by passage onto a moving chilled conveyer of steel molds, in which the melt cools to a semitransparent solid. If the hot melt is sprayed with a stream of cold water, it is shattered into fragments. The fragments are either charged into grinding and screening equipment to yield solid sodium silicates (granular) or are passed into a rotary dissolver. Here the solid material is dissolved by superheated (80-psi) steam. In some plants the hot melt from the furnace is passed directly into water, in which it is dissolved with steam. The resulting solution is clarified by settling in a tank and is adjusted to the desired specific gravity. Gravities range from 22 to 69°Bé, with 40°Bé the most common. The adjusted solution is sent to storage, whence it is charged into drums and tank cars.

Dry, powdered sodium silicate may be produced by taking liquors of proper specific gravities and forcing them through a very fine opening into a solidification chamber. The chamber is swept by a rapid current of cold air, which carries off the moisture. The desired sodium silicate is obtained by varying the ratio of the raw materials charged as well as by working up the proper solution.

Sodium silicate solutions may be treated with a mineral acid (sulfuric or hydrochloric acid) to yield hydrous silica and silicic acid. After the product is washed with water and dehydrated, silica gel results.

Use Pattern

	Per cent
Detergents and metal cleaning	45
Adhesives, sizing, and coatings	35
Miscellaneous, including silica gel	20
	100



Price—Sodium Silicate

Miscellaneous

Properties. *Sodium Tetrasilicate* ($Na_2Si_4O_9$ or $Na_2O \cdot 3.9SiO_2$), water glass. Amorphous white deliquescent powder and lumps or clear to cloudy, colorless aqueous solutions of varying densities and viscosities.

Mol. wt.	302.23	M.P.	1,100°C (liquid temperature)

Soluble in hot and cold water. Insoluble in alcohol. The colloidal silicates or water glasses vary in chemical composition from $Na_2O \cdot 1.6SiO_2$ to $Na_2O \cdot 4SiO_2$. A solution containing 32 per cent $Na_2O \cdot 1.69SiO_2$ has a specific gravity of 1.365 20°C/4 (38.8°Bé) and a viscosity of 29 centiposes (20°C); a 32 per cent $Na_2O \cdot 3.9SiO_2$ solution has a specific gravity of 1.298 20°C/4 (33.3°Bé) and a viscosity of 180 centiposes (20°C).

Sodium Disilicate ($Na_2Si_2O_5$). Rhombic, pearly luster, crystals.

Mol. wt.	182.11	M.P.	874°C

Soluble in hot and cold water.

Sodium Metasilicate (Na_2SiO_3). Monoclinic, colorless crystals or white powder containing approximately 51.7 per cent Na_2O and 46.2 per cent SiO_2.

Mol. wt.	122.05	M.P.	1,088°C
Sp. gr.	2.4		

Soluble in cold and hot water, decomposing in the latter. Insoluble in alcohol. Crystallizes from water as the pentahydrate and nonohydrate.

Sodium Metasilicate Pentahydrate ($Na_2SiO_3 \cdot 5H_2O$). White, granular or crystalline material containing about 29.2 per cent Na_2O and 28.7 per cent SiO_2.

Mol. wt.	212.10	M.P.	71.8°C

Very soluble in cold and hot water.

Sodium Metasilicate Nonohydrate ($Na_2SiO_3 \cdot 9H_2O$). White, efflorescent rhombic crystals.

Mol. wt.	284.20	M.P.	40–48°C
		B.P.	Loses $6H_2O$, 100°C

Very soluble in cold and hot water; soluble (29 per cent) in $N/2$ sodium hydroxide at 18°C. Insoluble in alcohol and acids.

Sodium Sesquisilicate ($Na_3HSiO_4 \cdot 5H_2O$ or $Na_4SiO_4 \cdot Na_2SiO_3 \cdot 11H_2O$). White, granular powder containing approximately 36 per cent Na_2O and 24 per cent SiO_2.

M.P.	90–95°C

*p*H—11.6 (concentration of 0.1 per cent by weight). Soluble in water.

Sodium Orthosilicate (Na_4SiO_4). White, hexagonal crystals or powder.

Mol. wt. 184.05 M.P. 1,018°C

Soluble in water.

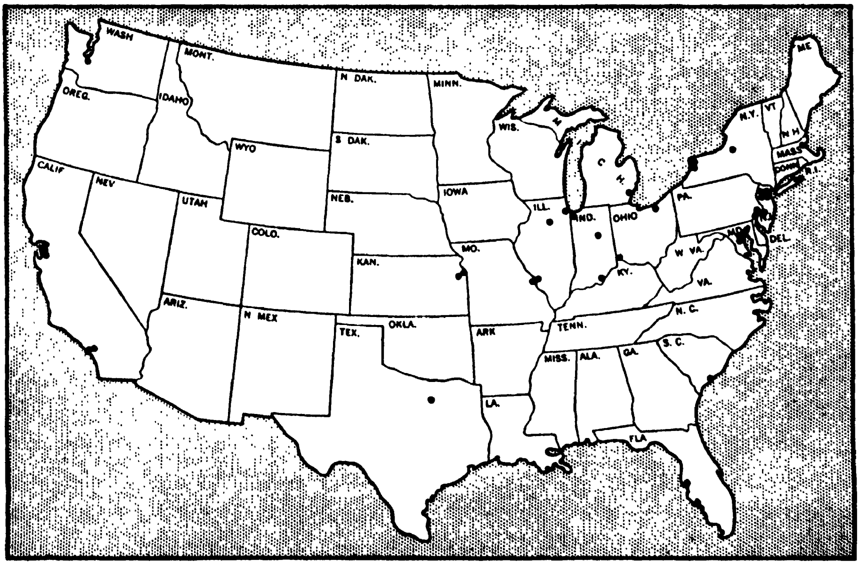
Grades. Solid, C.P., pure crystal, crude lumps, and powder. Solution: water-white and cloudy of various concentrations ranging from 22 to 69°Bé, having viscosities ranging from thin watery liquids to semiliquids. Common grades are 40 and 60°Bé.

Containers and Regulations. Solid and powder: drums, barrels, bags, cans, and bottles. Solutions: tank cars, drums, barrels, and bottles. No ICC shipping label required.

Economic Aspects

A wide variety of sodium silicates are manufactured and sold commercially. Products vary from those containing 1 mole Na_2O to 4 moles SiO_2 (water glass) to those containing 2 moles Na_2O to 1 mole SiO_2 (the orthosilicate). The most important is the metasilicate, which contains equimolar quantities of Na_2O and SiO_2.

Plants are quite simple, and adjustment of raw-material ratios and furnace conditions alters the nature of the product made. The smallest economic plant size is a function of furnace size. As with other furnace products, continuous operation is required because of the premature failure of the refractory if the furnace is alternately heated and cooled.



Location of Sodium Silicate Plants

Many users of sodium silicate (such as soap manufacturers) manufacture their own sodium silicate, but only the comparatively large user can save money by this procedure. Recent increased requirements for silica gel catalysts, particularly for the oil industry, may result in increased plant capacity.

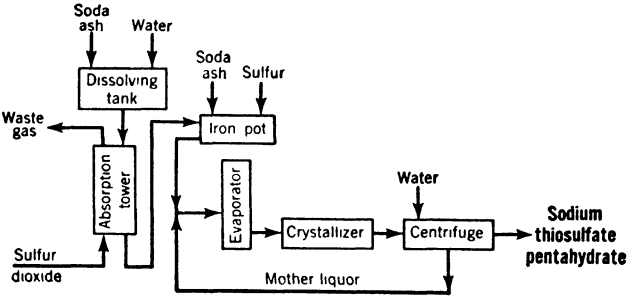
A small plant would be one manufacturing 2,000 tons of 40°Bé sodium silicate annually. Such a plant would cost about $8 per annual ton capacity. A large plant would have an annual capacity of about 50,000 tons.

SODIUM THIOSULFATE

(HYPO)

$Na_2S_2O_3 \cdot 5H_2O$

From Soda Ash and Sulfur Dioxide



Reaction

$$Na_2CO_3 + H_2O + 2SO_2 \rightarrow 2NaHSO_3 + CO_2$$

$$2NaHSO_3 + Na_2CO_3 + 2S \rightarrow 2Na_2S_2O_3 + H_2O + CO_2$$

Material Requirements (Theoretical)

Basis—1 ton sodium thiosulfate pentahydrate

Soda ash (Na_2CO_3)	850 lb
Sulfur dioxide	520 lb
Sulfur	260 lb

Process

A 26° Bé soda-ash solution is allowed to percolate downward through a series of absorption towers countercurrent to sulfur dioxide gas. The towers are usually lead-lined, packed with wood slats, and supported by acid-proof brick. The solution leaving the bottom of the last tower is chiefly sodium bisulfite (22 per cent SO_2 content). The solution is run into a ceramic-lined cast-iron pot fitted with an agitator. Sufficient soda ash is added to convert the bisulfite to neutral sodium sulfite. Sulfur is then added, and the contents of the kettle are heated to boiling. The resulting sodium thiosulfate solution is pumped to a steam-heated evaporator where it is concentrated to 51°Bé. The hot liquor from the evaporator is then cooled, crystallized, and centrifuged in the conventional manner.

Sodium thiosulfate crystals are efflorescent and must be packed at once in moisture-tight containers.

From Sodium Sulfite and Sulfur

In many plants the starting material for sodium thiosulfate manufacture is sodium sulfite. In such cases the plants are essentially the same as that described beginning with the cast-iron reaction kettle.

From By-Product Sodium Sulfide

In the manufacture of sodium sulfide, a by-product sulfide–carbonate liquor (8 per cent sodium sulfide, 6 per cent sodium carbonate) is obtained, which may be converted to sodium thiosulfate by reaction with sulfur dioxide. The reaction taking place is essentially as follows:

$$2Na_2S + Na_2CO_3 + 4SO_2 \rightarrow 3Na_2S_2O_3 + CO_2$$

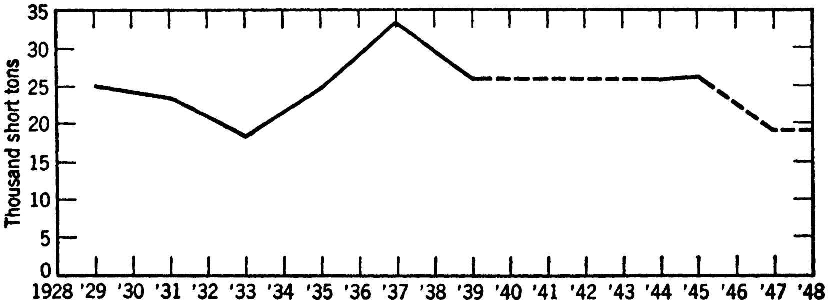
Any excess sodium sulfide reacts with sulfur dioxide to yield sodium sulfite:

$$Na_2S + SO_2 + H_2O \rightarrow Na_2SO_3 + H_2S$$

In such a case the sulfite may be converted to the thiosulfate by treatment with sulfur. Accordingly, the plant used to produce sodium thiosulfate from by-product sodium sulfide is almost identical with that described using soda ash, sulfur dioxide, and sulfur.

From By-Product of Sulfur-Dye Manufacture

In the manufacture of sulfur dyes by fusion of sulfur, caustic soda, and certain organic compounds, the fusion product is leached with water,

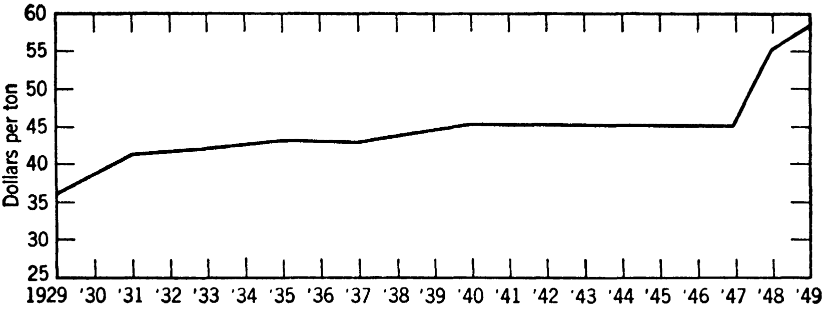


Production—Sodium Thiosulfate

and the leach liquor is filtered to remove the insoluble dye. The filtrate resulting from this process contains most of the original sulfur and caustic soda in the form of sodium thiosulfate. This filtrate may be concentrated and crystallized to yield sodium thiosulfate of good quality.

Use Pattern

	Per cent
Photography	75
Bleaching pulp, paper, and textiles Tanning Mordant	25
	100



Price—Sodium Thiosulfate

Miscellaneous

Properties. White, translucent, monoclinic crystals having a cooling taste but leaving a bitter aftertaste.

Mol. wt.	248.19	M.P.	Decomposes 48°C
Sp. gr.	1.685		

Soluble in water (74.7 g per 100 g at 0°C, 301.8 g per 100 g at 60°C), and ammonia. Very slightly soluble in alcohol.

Anhydrous Sodium Thiosulfate ($Na_2S_2O_3$) is the less common form and has the following properties: White, monoclinic crystals.

Mol. wt.	158.11
Sp. gr.	1.667

Soluble in water (50 g per 100 g at 0°C, 231 g per 100 g at 80°C).

Grades. USP, C.P., commercial, and pure in crystal and granular forms.

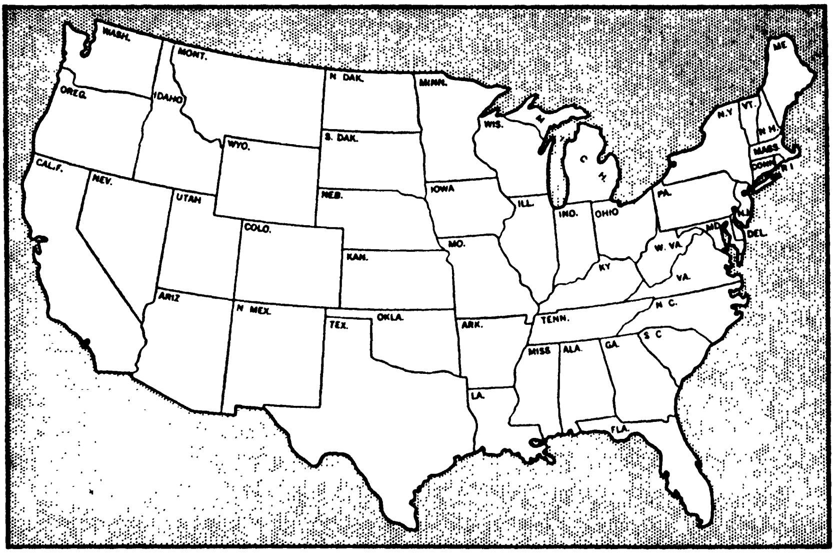
Containers and Regulations. Casks, barrels, kegs, boxes, and bottles. No ICC shipping label required.

Economic Aspects

Sodium thiosulfate, $Na_2S_2O_3 \cdot 5H_2O$ (commonly called "hypo"), is often confused with sodium hyposulfite ($Na_2S_2O_4 \cdot 2H_2O$), which in turn is sold commercially as sodium hydrosulfite. The latter is a powerful reducing agent, whereas sodium thiosulfate may be classified as a mild reducing agent. The uses of sodium thiosulfate center around its ability to dissolve silver salts; accordingly, the largest quantities are used in photography.

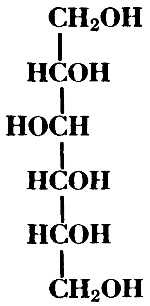
Major production is derived from sulfide liquors formed as a by-product in the manufacture of either sodium sulfide or sulfur dyes. Small producers normally use the soda-ash–sulfur dioxide process. Equipment requirements in either case are quite small.

No marked changes in either consumption or use are foreseen in the near future. If such a change does occur, present producers will have no difficulty in expanding production.



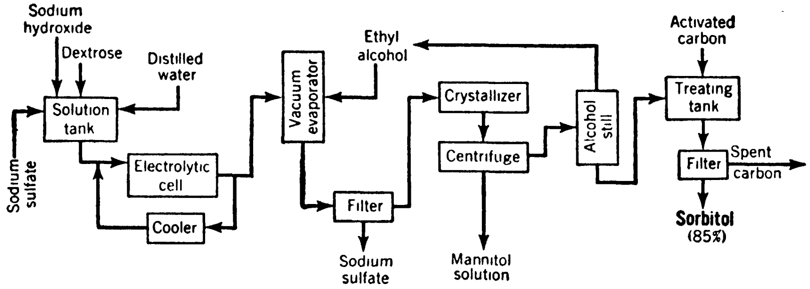
Location of Sodium Thiosulfate Plants

SORBITOL

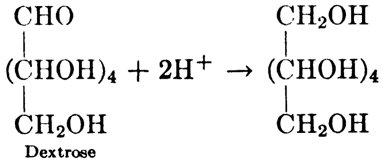


$$\begin{array}{c} \mathrm{CH_2OH} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{HOCH} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{HCOH} \\ | \\ \mathrm{CH_2OH} \end{array}$$

From Dextrose by Electrolytic Reduction



Reaction



$$\begin{array}{ccc} \mathrm{CHO} & & \mathrm{CH_2OH} \\ | & & | \\ \mathrm{(CHOH)_4} + 2\mathrm{H}^+ & \rightarrow & \mathrm{(CHOH)_4} \\ | & & | \\ \mathrm{CH_2OH} & & \mathrm{CH_2OH} \\ \text{Dextrose} & & \end{array}$$

90% yield (both mannitol and sorbitol)

25–50% current efficiency

Material and Utility Requirements

Basis—1 ton sorbitol (85%)

Dextrose	2,000 lb	Activated carbon	45 lb
Sodium hydroxide	Small	Electricity	Figures not available
Sodium sulfate	525 lb (less recovery)	Ethyl alcohol	Losses only

Process

Dextrose, which is also known as *d*-glucose or corn sugar, is reduced electrolytically to produce the hexahydric alcohol: sorbitol.

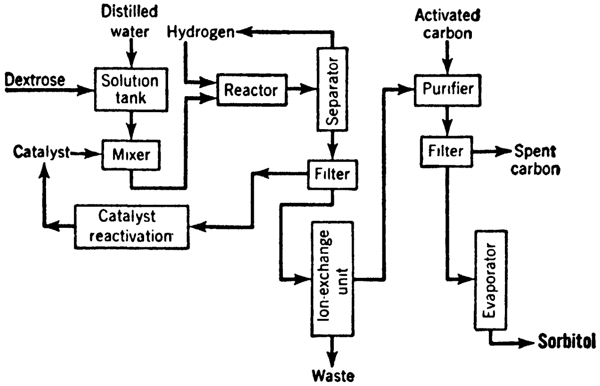
A solution of dextrose and distilled water (325 g dextrose per l) is charged into a large, mechanically agitated dissolving tank. To the concentrated aqueous solution is added enough sodium hydroxide and sodium sulfate (85 gpl) to render the solution alkaline and make it an electric conductor. The prepared solution is then run into electrolytic cells fitted with pure lead anodes and lead-mercury-amalgam cathodes. Each anode is surrounded by a diaphragm of unglazed porcelain, which separates the dilute sulfuric acid (resulting from the sodium sulfate) from the dextrose solution.

Direct current, supplied by motor-generator units, is applied at a cathode current density of 1 ampere per square decimeter to liberate nascent hydrogen at the cathode and nascent oxygen at the anode. The latter forms lead peroxide, the process by-product, while the nascent hydrogen reduces the dextrose to sorbitol. The electrolytic solution is circulated through a cooler to maintain a constant reaction temperature. Room temperature is optimum for the reaction, which requires about one week to complete. The *p*H of the catholyte gradually rises from 7.0 to 12.6, at which point sulfuric acid is added.

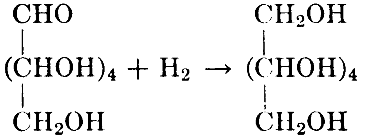
The crude sorbitol solution is pumped into a glass-lined, steam-jacketed vacuum evaporator where water is removed. The residue, consisting of sorbitol, sodium sulfate, and some of the stereoisomer, mannitol, is dissolved in hot ethyl alcohol. The insoluble sodium sulfate is removed by filtration, and the alcoholic filtrate is run into a crystallizer, where the temperature is lowered sufficiently to crystallize out the mannitol. The cell operations may be varied to produce various amounts of mannitol, but, in general, the yield is kept fairly low. After the cool mixture is centrifuged, the crude sorbitol solution is passed into a steam-jacketed kettle still. Here the alcohol is distilled off, condensed, and returned to the vacuum evaporator for re-use. The crude sorbitol sirup is given a decolorizing and purifying treatment with activated carbon. The carbon is removed by filtration to give commercial 83 to 85 per cent sorbitol. The remainder of the product is chiefly water with small amounts of dextrose, stereoisomers, and sodium sulfate as impurities. A technical 70 per cent aqueous solution is also prepared by further purification and dilution. Crystalline *d*-sorbitol is also produced commercially and is prepared by crystallizing a pure sorbitol solution, free from related polyhydric bodies and impurities. The powder contains over 99 per cent sorbitol.

Zinc cathodes may be used in place of amalgamated-lead cathodes, in which case it is claimed that higher current efficiencies may be obtained and mannitol production can be practically eliminated.

From Dextrose by Catalytic Hydrogenation



Reaction



$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} + H_2 \rightarrow \begin{array}{c} CH_2OH \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

Dextrose

95% yield

Material Requirements

Basis—1 ton sorbitol (85%)

Dextrose	1,900 lb
Hydrogen (STP)	5,000 cu ft
Catalyst loss (nickel)	2–3 lb
Activated carbon	20–30 lb
Acid and alkali for ion-exchange resin regeneration	Variable

Process

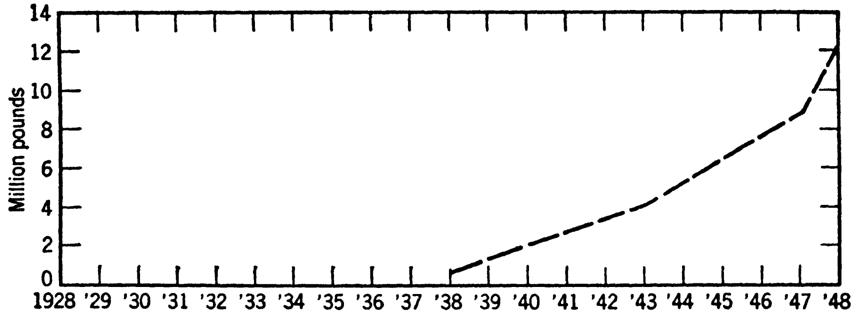
The catalytic hydrogenation of dextrose yields sorbitol.

Dextrose is dissolved in warm distilled water so that a concentrated solution results. From the dissolver the solution is fed into a weigh-tank mixer, where finely powdered nickel (1 part), supported on clay or diatomaceous earth (4 parts), is added as the catalyst. The resulting slurry is fed into a continuous reactor at a pressure of 100 to 125 atm.

Hydrogen, compressed to about 175 atm, is bubbled into the vertical-tube reactor with the slurry. Reaction temperature may vary from 280 to 400°F. The reactants pass through the reactor in a matter of minutes and are discharged into a tank, where the excess hydrogen is removed for recompression and recycling.

The sorbitol-spent catalyst slurry is filtered in a pressure leaf filter. The separated catalyst is reprocessed and re-used. The clear crude sorbitol solution is passed through a two-stage ion-exchange unit containing organic ion-exchange resins. Metallic cations are removed in the first stage, and anions are absorbed in the second. All process equipment prior to this step is constructed of ordinary steel. The demineralizer itself is rubber-lined, and subsequent equipment is either stainless steel or stainless-clad steel to insure freedom from impurities.

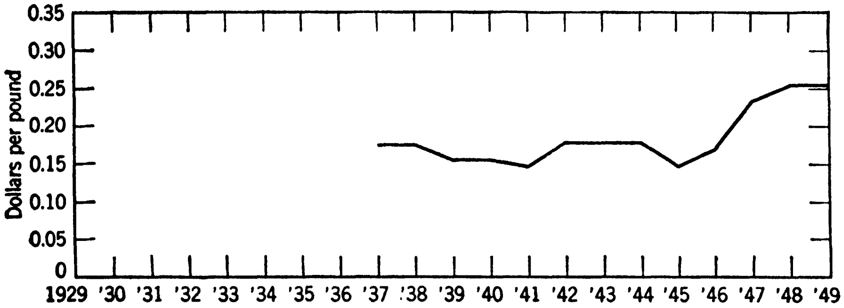
The treated solution is then purified and decolorized by activated carbon which is subsequently removed by filtration. The purified dilute (about 50 per cent) sorbitol solution is fed into a single-effect continuous evaporator, where at about 200°F and 27.5 in. Hg vacuum the solution is concentrated. Sorbitol of 70 per cent concentration results, which is then ready for shipment. Commercial 85 per cent and crystalline sorbitol may be prepared from the 70 per cent solution.



Production—Sorbitol (Estimated)

Use Pattern

	1947 (est.), per cent
Ascorbic acid	30
Humectant	30
Miscellaneous, including resins, printing, gelatin and glue extenders	40
	100



Price—Sorbitol

Miscellaneous

Properties. White, odorless, crystalline powder having a sweet, cooling taste. Ordinarily contains ½ molecule of water.

Mol. wt.	182.17	M.P.	97.7°C
Sp. gr.	1.472 (−5°C)		

Very soluble in water and slightly soluble in methyl alcohol, aliphatic amines, phenol, and glacial acetic acid. Very slightly soluble in alcohol. Insoluble in ether and most other common organic solvents.

Grades. Commercial crystals, technical solution (70 per cent in water), and commercial solution (a noncrystallizing 83 to 85 per cent sirup). The 85 per cent commercial solution has a specific gravity of 1.35 and a viscosity at 25°C of 7,400 cp.

Containers and Regulations. Crystals: barrels, tins, and bottles. Solutions: drums, tins, and bottles. No ICC shipping label required.

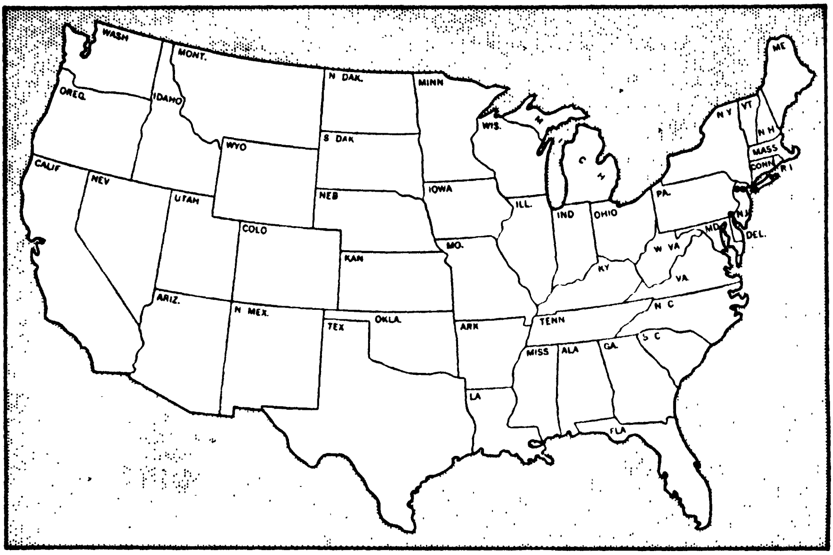
Economic Aspects

The first large-scale organic electrolytic-reduction plant was built in 1937 for the production of mannitol and sorbitol from dextrose. Recently built plants, however, have been of the high-pressure hydrogenation type, in which only the one isomer, sorbitol, is produced. In general, organic electrolytic processes are slow and expensive, particularly with regard to labor and maintenance, and cannot compete with other synthetic methods.

Sorbitol appears to have a definite place in the higher-alcohol field and competes generally with the glycols and glycerine. The chief single use to date, as shown in the use pattern, is for the manufacture of ascorbic acid (vitamin C). In recent years, sorbitol has made more and more inroads in former glycerine fields, chiefly in the tobacco, polyhydric ester, and printing fields. Use as a tobacco humectant, particularly, has increased markedly.

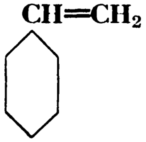
Mannitol, the joint product of electrolytic sorbitol production, is not yet nearly so generally useful. It has possibilities, however, in the explosives field; minor amounts were so used during World War II.

The cost of an electrolytic plant of 3,000,000 lb annual capacity is estimated as $1,250,000. Sufficient details are not known concerning the catalytic hydrogenation plant to make an accurate estimate of plant cost.

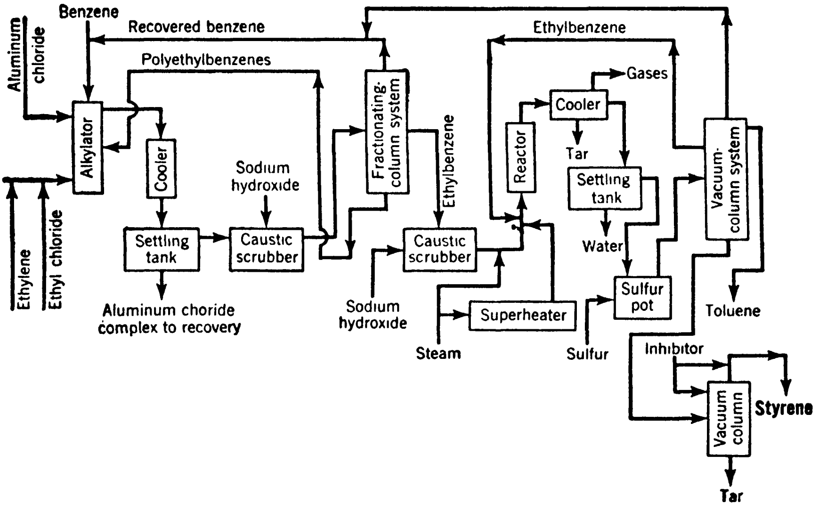


Location of Sorbitol Plants

STYRENE



From Benzene and Ethylene (Ethylbenzene)



Reaction

$$C_6H_6 + CH_2{=}CH_2 \xrightarrow{AlCl_3} C_6H_5CH_2CH_3$$

$$C_6H_5CH_2CH_3 \xrightarrow{\text{Catalyst}} C_6H_5CH{=}CH_2 + H_2$$

86–92% yield

Material Requirements (Major)

Basis—1 ton styrene

Benzene	1,730 lb	Aluminum chloride	20 lb
Ethylene	640 lb	Ethyl chloride	Small

Process

Benzene is alkylated with ethylene in the presence of an aluminum chloride or phosphoric-acid catalyst. The resulting ethylbenzene is catalytically dehydrogenated in the presence of steam or benzene to yield styrene.

Dry benzene (99 per cent) and ethylene (95 per cent) are continuously fed into an alkylating tower operating at essentially atmospheric pressure. A small amount of ethyl chloride is added to the ethylene feed as a source of hydrogen chloride (as well as ethylene), which acts as a catalyst promoter. Granular aluminum chloride (97.5 per cent) is fed to the top of the alkylator at a constant rate. The reactant ratio is about 0.6 mole of ethylene per mole of benzene. No ethylene is recycled, and the losses to the vents are negligible. From 75 to 100 lb of ethylbenzene may be obtained per lb of aluminum chloride catalyst.

The exothermic alkylation reaction is maintained at approximately 95°C by cooling water. The aluminum chloride combines with the hydrocarbon (benzene and ethylbenzene) to form a hydrocarbon-insoluble complex (reddish-brown oil). The reaction products (crude alkylate plus entrained complex) are led to coolers, where the temperature is reduced to about 40°C. Here the aluminum chloride complex is separated from the crude mixture in settling tanks and is pumped back to the alkylator or to a high-temperature dealkylator. The latter, operating at 200°C, breaks down a charge of complex polyethylbenzenes to benzene and ethylbenzene (which are returned to the system) and a tarry aluminum chloride residue. Approximately 80 per cent of the aluminum chloride may be recovered.

The crude ethylbenzene from the settling tanks is sent to a caustic scrubbing system for neutralization. After being washed with a 50 per cent caustic solution, the "sweetened" material is charged to a fractionating system. The crude alkylate enters an atmospheric stripping column where the polyethylbenzenes are removed from the bottom (200°C) and are distilled in a vacuum column at 50 mm pressure. Here, at 135°C head temperature, the polyethylbenzenes are fractionated, and the heads are combined with the bottoms from the ethylbenzene column and sent back to the alkylator for dealkylation. The bottoms are sent to the afore-mentioned high-temperature dealkylator.

The overhead from the stripper (135°C) containing benzene and ethylbenzene is sent to a benzene column, where the benzene is removed. After an azeotropic distillation to remove the water, the dry benzene is returned to the alkylator feed line. The bottoms from the benzene column are sent to an ethylbenzene column. At a head temperature of 138°C, ethylbenzene at a purity greater than 99 per cent is obtained.

The material is scrubbed with 20 per cent aqueous sodium hydroxide and dried by percolation through a bed of flake caustic.

Purified ethylbenzene is preheated with steam (to 160°C) and by heat interchange (to 520°C). Superheated steam (710°C) and the ethylbenzene vapors are continuously mixed and fed into a reactor in a ratio of 2.6 lb steam per lb ethylbenzene. The reactor contains a selective fixed dehydrogenation catalyst such as zinc, chromium, iron, or magnesium oxide, on activated charcoals, aluminas, or bauxites. The catalyst operates continuously and has a long life (about 1 yr). At a catalyst temperature of about 630°C (resulting from the vapor-feed temperature), conversions of 35 to 40 per cent per pass may be realized.

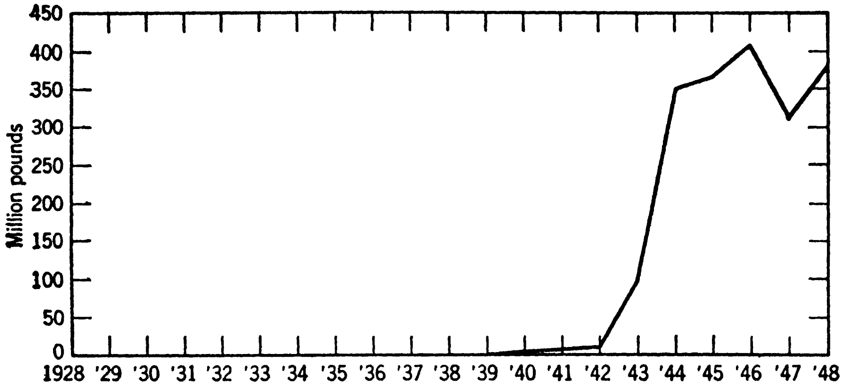
The reaction product leaves the top of the reactor at about 565°C and is cooled first by the incoming ethylbenzene and then by steam in heat exchangers. A spray-type cooler lowers the product temperature to about 105°C and condenses out tars. A final condenser liquefies the steam, styrene, toluene, and benzene, while the vent gases containing hydrogen, carbon monoxide, carbon dioxide, and lower aliphatic hydrocarbons are sent to a refrigerated recovery system. The condensed materials pass to a settling tank, where the hydrocarbons are decanted and the water is discharged to a disposal system.

The crude styrene of average composition (37 per cent styrene, 61 per cent ethylbenzene, 1 per cent toluene, 0.7 per cent benzene, and 0.3 per cent tar) is passed through a pot containing sulfur. This stream (containing enough dissolved sulfur to act as a polymerization inhibitor) is preheated and then fed to vacuum columns. At 157 mm pressure, benzene and toluene distil at a head temperature of 57°C. These materials are separated by distillation, and the benzene is recycled to the alkylator. The toluene is run to storage.

The column bottoms (90°C) containing styrene, ethylbenzene, and tar are passed successively to primary and secondary vacuum columns. By operating at 35 mm pressure and a bottom temperature of 90°C (higher temperatures accelerate polymerization), ethylbenzene is separated from the styrene and recycled to the reactor. Styrene is distilled in the second column to remove tar and sulfur. A polymerization inhibitor is added to the top of the column. The tarry residue discharged from the bottom is burned. The distilled styrene passes to receivers, where more inhibitor (paratertiary butyl catechol) is added to bring the concentration to 10 ppm. The finished material is refrigerated below 20°C and loaded to insulated tank cars. Styrene (99.7 to 99.9 per cent) is obtained in an over-all yield of about 86.5 per cent based on the weight of benzene and ethylene. The yield of benzene to ethylbenzene averages 95.5 per cent, whereas that of ethylene to ethylbenzene averages 96.8

per cent. The yield of styrene based on ethylbenzene is about 90 per cent.

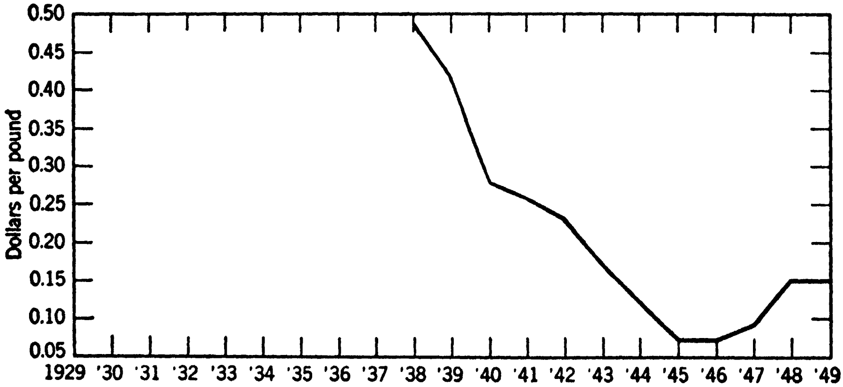
Styrene is commercially produced entirely from ethylbenzene. Most of the ethylbenzene is manufactured by the afore-mentioned process. It may also be made by the reaction of ethyl alcohol (95 per cent) and benzene in the presence of phosphoric acid at temperatures around 315°C and pressures of about 250 psi. This catalyst may also be used for the ethylene–benzene reaction.



Production—Styrene

Use Pattern

	1947 (est.), per cent
Synthetic rubber	66
Resins	34
	100



Price—Styrene

Miscellaneous

Properties. Colorless to yellowish, highly refractive oily liquid with a characteristic aromatic odor. Polymerizes slowly on standing, rapidly on heating, becoming increasingly viscous until a clear, glassy, solid state is reached.

Mol. wt.	104.14	M.P.	−30.6°C
Sp. gr.	0.903 20°C/4	B.P.	145.2°C

Weight per gallon 7.55 lb (20°C)

Soluble in alcohol and ether. Insoluble in water.

Flash point (closed cup)	90°F
Ignition temperature	914°F
Vapor density (air = 1)	3.60
Explosive limits (% by volume in air)	Lower 1.1 Upper 6.1

Grades. Technical (99 per cent).

Containers and Regulations. Tank cars, drums, cans, and bottles (containing a stabilizer). No ICC shipping label required.

Economic Aspects

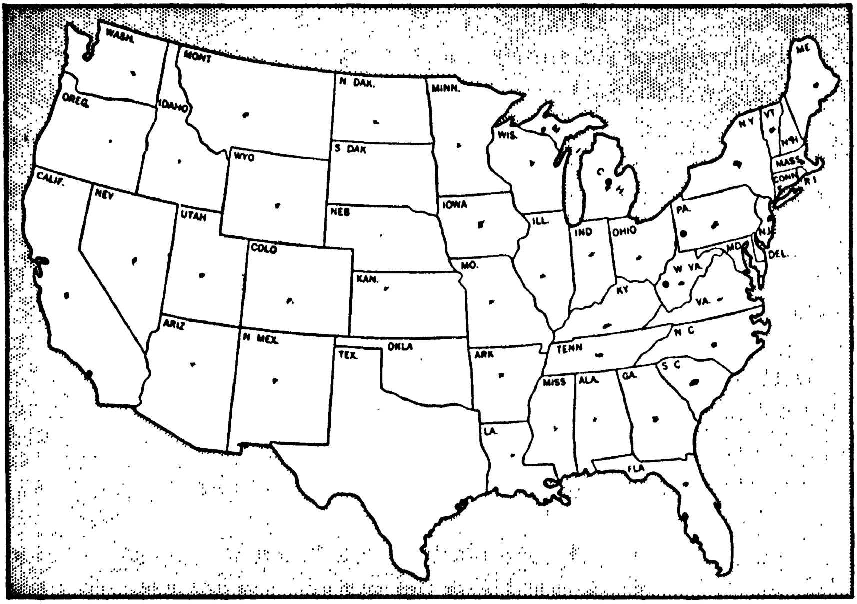
Styrene production like that of butadiene soared during World War II because of the requirements of the synthetic-rubber program. Approximately 500 lb styrene are required per long ton of GR-S (Buna S). Considerable work has been done toward the substitution of other materials for styrene, in order to produce a synthetic elastomer superior to Buna S. Both vinyl pyridine and chlorinated styrene have shown promise but have not been sufficiently better than styrene to warrant large-scale development. On the other hand, copolymers of butadiene with high styrene content show considerable promise in the plastics and coating fields.

Before the war polystyrene plastics were becoming popular. Large-scale production of styrene during the war and the accompanying possibility of lower costs will undoubtedly lead to increased plastic use in the future. Already polystrene is the cheapest of all rigid thermoplastic materials. For many uses, polystyrene plastics are competitive with cellulose acetate. Their excellent electrical properties, high clarity, and high water and chemical resistance will lead to much greater popularity. A limitation on use is a working-temperature ceiling of 176°F. Materials similar to the plastic armor, Doron (a polyester styrene resin), will probably see expanded use.

There are also indications that styrene may find a considerable market in the nonplastic field. Among these nonplastic uses are the impregnation of magnesium castings and the replacement of drying oils in paints.

. It should be realized that large-scale production of styrene is a comparatively recent achievement. Accordingly, process changes and new developments may alter the commercial process somewhat in the next several years. That the process described is fundamentally sound is borne out by the rapid increase in production in the critical period of World War II.

Styrene plants built for the Government during the war varied in initial rated capacity from 25,000 to 50,000 tons per year, but, after bottlenecks were ironed out, capacities were increased on the average by about 50 per cent. One private plant had a capacity of 10,000 tons annually. Plant investment varies from $200 to $400 per annual ton, depending on plant size and the process used.

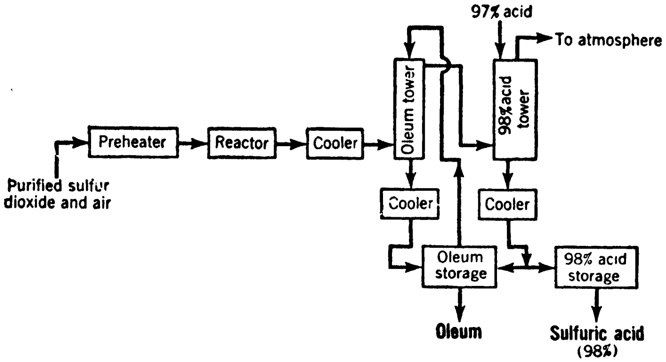


Location of Styrene Plants

SULFURIC ACID

H_2SO_4

Contact Process



Reaction

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$SO_3 + H_2$[redacted]

96–98% conversion

92–96% yield (sulfur)

Labor, Heat, and Material Requirements

Basis—1 ton sulfuric acid (100 per cent)
in plant of 50 tons per day capacity

Sulfur	688 lb	Electricity	5 kw-hr
Water	4,000 gal	Labor	0.64 man-hr
Steam *	200 lb	Air	250,000 cu ft

Process

A purified, dry sulfur dioxide gas mixture containing 7 to 10 per cent sulfur dioxide and 11 to 14 per cent oxygen is passed through a preheater (heat exchanger) to a steel reactor (converter), containing a plat-

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* Furnished by waste heat boiler or heat exchanger (preheater).

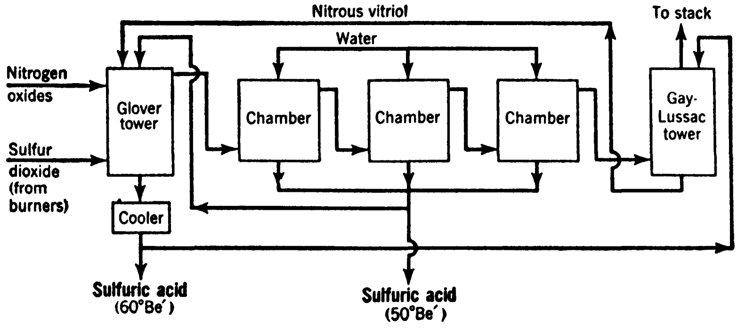
inum or vanadium pentoxide catalyst. The way the catalyst is arranged within the reactor and whether the heat exchangers are internal or external vary from one plant to another. In general, the incoming gases are heated indirectly by the hot gaseous products: the temperature in the first part of the reactor is 500 to 600°C for rapid reaction and is then lowered by entering gases; the temperature in the second part of the reactor is 400 to 450°C, so as to obtain a suitable equilibrium constant. The contact time varies with design but is generally 2 to 4 sec.

The gases from the reactor are partially cooled by passage through a heat exchanger and finally cooled to about 100°C in going through a cooler. The gas, containing about 95 per cent of its sulfur as sulfur trioxide, is sent to an internally cooled oleum tower (constructed of brick and packed with quartz), where part of the sulfur trioxide is absorbed in the oleum, which is fed to the tower at such a rate that a rise of not over 0.5 to 1.0 per cent in acid strength occurs. The gas then passes to another cooled tower, where the remaining sulfur trioxide is scrubbed with 97 per cent acid fed at a rate that allows about 1 per cent increase in acid strength. Proper choice of acid concentrations, tower temperature, and blending of the products allows production of various concentrations of acid (above 97 per cent) and oleum (up to 40 per cent free SO_3). Higher-strength oleum (65 per cent) is prepared by distilling 20 per cent oleum. Acid less than 97 per cent concentration cannot be used for scrubbing sulfur trioxide-containing gases because of mist formation and consequent sulfur trioxide losses.

The platinum catalyst is prepared by depositing finely divided platinum on a carrier such as silica gel, calcined magnesium sulfate, or asbestos. For example, platinized silica gel may be prepared by impregnating the gel with a solution of ammonium chloroplatinate to give a mass containing about 0.1 per cent platinum, which gives sulfur dioxide conversions of about 96 per cent. This catalyst requires about 1.5 to 3.5 oz of platinum per daily ton of 100 per cent sulfuric acid; 90 per cent recovery of the original platinum is realized when the mass is discarded.

Soluble vanadium compounds such as ammonium vanadate or vanadium pentoxide are deposited on a carrier such as zeolite or kieselguhr, and the resulting mass is pelleted. This catalyst acts similarly to the platinum catalyst, giving conversions of about 97 per cent; about 20 lb of catalyst mass is used per daily ton of 100 per cent acid.

Chamber Process



Reaction

$$2NO + O_2 \rightarrow 2NO_2$$

$$NO_2 + SO_2 + H_2O \rightarrow H_2SO_4 + NO$$

98–99% conversion

92–96% yield (sulfur)

Labor, Heat, and Material Requirements

Basis—1 ton sulfuric acid (100 %)
in plant of 50 tons per day capacity

Sulfur	677 lb	Water	2,500 gal
Nitrogen oxides (as anhydrous ammonia)	5 lb	Air	275,000 cu ft
		Electricity	15 kw-hr
		Labor	1.1 man-hr

Process

Hot sulfur dioxide gases (425 to 600°C) from the burners (7 to 9 per cent sulfur dioxide and 9 to 12 per cent oxygen) are introduced into the base of a Glover tower. The gases pass countercurrent to a cool stream of nitrous vitriol (72.8 per cent H_2SO_4), which has been diluted from 60°Bé (77.7 per cent H_2SO_4) acid obtained from the Gay-Lussac towers. The hot (100 to 140°C) Glover or "tower" acid (60°Bé) is cooled; part is used again in the Gay-Lussac tower, and the rest is sent to storage.

Partial oxidation (about 10 per cent) of the sulfur dioxide occurs near the top of the Glover tower where nitric oxide gas, generated by an ammonia oxidation unit (see *Nitric Acid*), is mixed with the sulfur dioxide gases; the resulting mixture (SO_2, SO_3, N_2, O_2, NO, NO_2, N_2O_3, and steam) leaves the tower at a temperature of 70 to 110°C and is sucked into the lead chambers by means of a fan. Here, the greater proportion of sulfur dioxide is oxidized to the trioxide and hydrated to sulfuric acid. Extra water is introduced as a spray, and the sulfuric acid formed condenses on the lead walls.

This chamber acid (62 to 68 per cent H_2SO_4), as it is called, is pumped to the Glover tower for concentration and nitrogen oxide removal. The gases leaving the chambers contain little sulfur dioxide but are led into the bottom of the Gay-Lussac tower (also packed), countercurrent to cold (35 to 40°C) 60°Bé (77.7 per cent) sulfuric acid, which strips nitrogen oxides from the gases, forming the nitrous vitriol containing 1 to 2.5 per cent N_2O_3 by weight. The nitrous vitriol is pumped to the top of the Glover tower. The stripped gases are led to a stack and discharged to the atmosphere.

The number of lead chambers varies from 3 to 12, and the size depends on their design. Boxlike chambers require 6 to 12 cu ft space per lb of sulfur burned per 24 hr, whereas externally water-cooled truncated cones (Mills-Packard type) require only 3 to 5 cu ft. With good operation the average chamber set lasts more than twenty years.

The chamber process produces directly a weaker acid of 50 to 60°Bé. Up to 66°Bé acid may be obtained by subsequent concentration.

Raw Materials

Both the contact and chamber processes for producing sulfuric acid utilize sulfur dioxide as the basic raw material. The primary difference in the processes is the method of oxidizing the sulfur dioxide to sulfur trioxide. However, the chamber process can more easily use sulfur dioxide of low purity and may, therefore, be better adapted to producing sulfuric acid from pyrites and waste gases.

The principal sources of sulfuric acid have been distributed as follows:

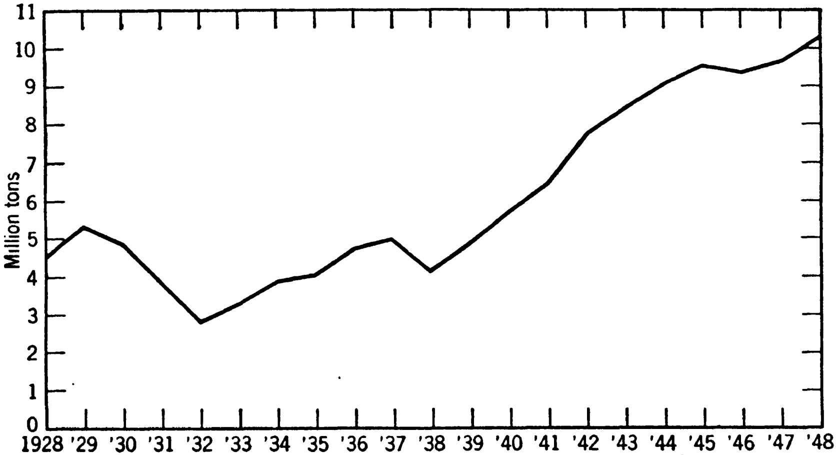
	Years, per cent	
Source	1939	1944
From sulfur	64.0	75.0
From pyrites	23.3	14.7
From smelters	11.9	9.6
From hydrogen sulfide	0.8	0.7
	100.0	100.0

From Sulfur. Deposits of sulfur or brimstone in the United States are mined by the Frasch process, which consists of melting the solid sulfur by superheated water and then forcing the molten material to the surface of the ground by the use of compressed air. The purity of the sulfur is very high (99.5 to 99.9 per cent), and, when burned with the proper ratio of air, it yields 7 to 10 per cent sulfur dioxide gas, which requires very little purification before use. In contact plants the gas is generally filtered and dried before it enters the reactor, whereas chamber plants do not require purified gas. Sulfur is usually shipped in the solid form, but some recent shipments of molten sulfur in insulated tank cars have been made to southern acid plants.

From Pyrites. Burner gases from iron pyrites (containing 42 to 45 per cent sulfur) require extensive purification, because the catalysts in the contact process are impaired by such impurities as dust, moisture, arsenic, chlorine, and fluorine. The purification includes dust removal, cooling, scrubbing, filtering, and drying. The chamber plants require only dust removal, but a purer grade of sulfuric acid is produced if some of the major impurities are removed.

From Smelters. The metallurgy of most nonferrous metals consists of roasting a sulfide ore to release waste gases containing sulfur dioxide. The waste gases of zinc smelters, most often used, must be given a treatment similar to pyrites gases to remove impurities.

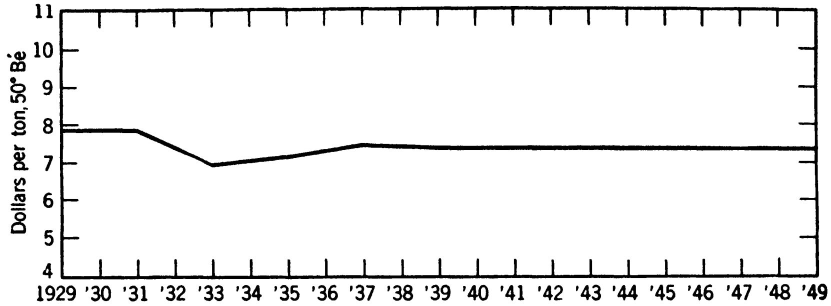
From Hydrogen Sulfide. This gas is removed in the purification of water gas, refinery gas, natural gas, and other fuel gases. The hydrogen sulfide is then burned in specially constructed furnaces to form sulfur dioxide. Other by-product sources are ferrous sulfate solutions from iron and steel pickling plants and "sludge acid" from oil refineries.



Production—Sulfuric Acid (100% H_2SO_4)

Use Pattern

	Per cent
Fertilizers	35
Petroleum refining	11
Chemicals	20
Iron and steel pickling	6
Coal products	6
Nonferrous metallurgy	3
Paints and pigments	7
Rayon and cellulose film	6
Industrial explosives	1
Textiles	1
Miscellaneous	4
	100



Price—Sulfuric Acid

Miscellaneous

Properties. Pure 100 per cent sulfuric acid is a colorless, odorless, heavy, oily liquid. It is referred to as monohydrate, since it may be regarded as being composed of equimolecular amounts of sulfur trioxide and water. It loses sulfur trioxide on heating until, at about 338°C, a constant-boiling acid of 98.3 per cent results.

Mol. wt.	98.08	M.P.	10.49°C
Sp. gr.	1.834 18°C/4	B.P.	340°C decomposes

Soluble in all proportions in water, producing a considerable amount of heat. One pound of 100 per cent sulfuric acid diluted to 90 per cent acid liberates 80 Btu and diluted to a 20 per cent concentration liberates 300 Btu.

Sulfuric acid is capable of dissolving large quantities of sulfur trioxide, producing various grades of oleum. When this solution (sulfuric acid–sulfur trioxide) is mixed with water the oxide combines with the water, forming more sulfuric acid.

Grades. Technical, C.P. and USP. The latter two grades are colorless and practically free of metallic and other impurities. The following table shows the various grades that are marketed to meet the requirements of the consuming industries.

Name of Grade	Percentage H_2SO_4	Specific Gravity at 15.6°C
Battery acid	33.5	1.250
50°Bé acid Fertilizer acid Chamber acid	62.2	1.526
60°Bé acid Tower acid Glover acid	77.67	1.706
60°Bé acid Oil of vitriol Concentrated acid	93.19	1.835
95% acid	95.0	1.841
98% acid	98.0	1.844
Monohydrate, H_2SO_4	100.0	1.835
20% Fuming or oleum 104.5% Acid	104.5—20% Free SO_3	1.927
40% Fuming or oleum 109% Acid	109.0—40% Free SO_3	1.965
65% Oleum	114.6—65% Free SO_3	1.990

Containers and Regulations. Tank cars, tank trucks, barrels, drums, carboys, and bottles. Since sulfuric acid is intensely corrosive and attacks practically all metals to some extent, container construction materials must be carefully chosen. Glass is utilized for all concentrations; rubber-lined and lead-lined containers may be used for dilute acids. Metals such as iron or steel and their alloys may be used for high acid concentrations (greater than 65°Bé). Freight shipments require a white ICC label.

Economic Aspects

Sulfuric-acid production is widely known as the "grandfather of all business indicators" for two reasons: its wide use in a variety of industries, and the rapid response of production to changes in consumption because of the hazard of storage in quantity and consequent low inventories.

For many years the chamber process was almost the only method used for the manufacture of sulfuric acid. Since the advent of the contact process, however, the chamber process has become less popular.

Very few new chamber plants have been built in the last twenty years, and these few are actually "modified" chamber plants. These plants rarely produce acid above 60°Bé, whereas the product of the contact plants is 98 and 100 per cent acid, which can be either diluted to lower concentrations or fortified with sulfur trioxide to yield fuming acid. Hence, a contact plant has much greater flexibility in acid strength than a chamber plant. On the other hand, chamber plants allow greater flexibility in production.

Both processes can use either brimstone or pyrites as alternative raw materials, with the choice dependent primarily on price. Higher purity and ease of handling have led to a gradual increase in brimstone use with a subsequent decrease in pyrites burned. In 1937, for instance, sulfuric-acid production was 64 per cent from brimstone, 24 per cent from pyrites, and 11 per cent from by-product gases. In 1947, these figures were 78 per cent, 12 per cent, and 10 per cent, respectively. In the same years, 47 and 69 per cent of the acid were produced by the contact process, and 53 and 31 per cent by chamber plants.

Competition between contact plants centers around the two catalysts used: metallic platinum- and vanadium-containing masses. Considerable controversy still exists concerning the merits of the two catalysts, but all new postwar contact plants are believed to use vanadium catalysts. In the chamber process, no new plants have been built recently using the old lead chambers. The new plants use either Mills-Packard chambers or packed towers (1 cu ft per lb sulfur per 24 hr).

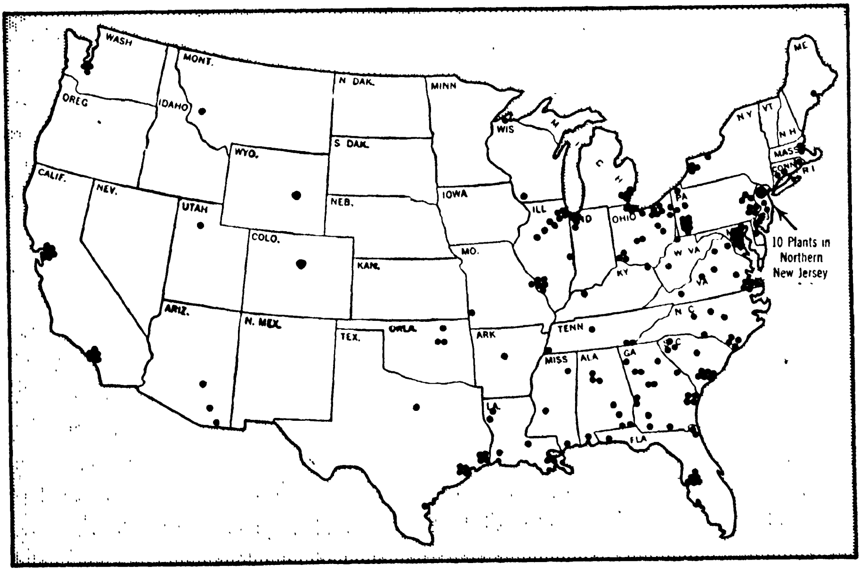
By-product processes make use of sulfur dioxide-containing gases from smelters, hydrogen sulfide-containing gases stripped from sour natural gas or from petroleum refineries, and by-product ferrous sulfate from steel pickling or titanium dioxide manufacture. An interesting future possibility is the use of sulfur dioxide recovered from power-plant flue gases. The development of an economic method for such recovery could change the entire raw-material picture. From time to time gypsum has been considered as a raw material for acid manufacture, or even as a replacement for sulfuric acid in many uses, but this threat has never materialized.

Sulfuric-acid plants are widely scattered throughout the United States, chiefly because of the low bulk value of the acid and subsequent high cost of shipment. Large users, such as fertilizer and explosives manufacturers, usually own and operate their own acid plants because they find it cheaper to make acid than to buy it.

The ordinary fertilizer factory may have a plant with a daily capacity of 30 to 60 tons 60°Bé acid. The minimum economic size of plants is generally considered to be 30 tons 60°Bé acid daily for chamber plants and 25 tons for contact plants (10,000 and 8,500 tons yearly, respectively). Plants in general vary in daily capacity from 100 tons of 100 per cent acid to 1,000 tons of 100 per cent acid. The largest-known *single* unit has a daily capacity of 500 tons. The capital investment required for a contact brimstone plant varies from $4,000 per ton for a 240-ton-per-day plant to $4,500 per ton for a 100-ton-per-day plant. Plants burning pyrites or by-product gases cost 20 to 25 per cent more. Recent contact plants have made use of outdoor construction with an estimated saving in construction of 7 per cent. A 100-ton 60°Bé chamber plant burning brimstone costs about $3,750 per daily ton.

Sulfuric acid is used so widely that a decrease in one use is often offset by an increase in another. Factors tending to decrease the use of sulfuric acid in the past 10 years are the obsolescence of the salt–sulfuric-acid process for manufacturing hydrochloric acid, partial replacement in the fertilizer industry by nitric and phosphoric acids, petroleum refining by hydrogenation, and the development of better reclaiming processes so that acid may be re-used. These are offset by new and increased uses in rayon and film manufacture, the increased manufacture of sodium alkyl sulfates as detergents, and the manufacture of hydrofluoric acid.

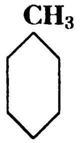
The handling of concentrated sulfuric acid is comparatively simple, compared to the handling of hydrochloric acid, since wrought iron or steel may be used. The development of tellurium lead and Duriron for hot dilute solutions has also solved what was once a difficult problem.



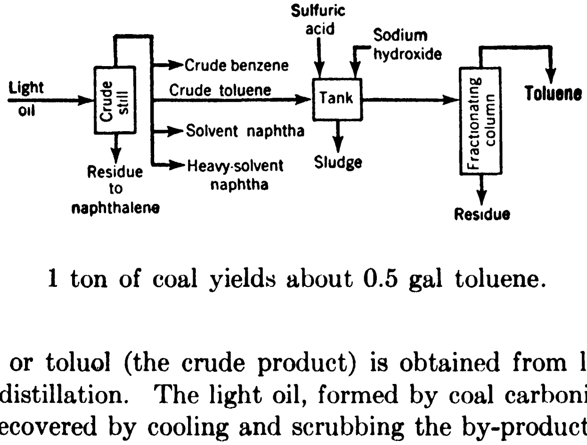
Location of Sulfuric-Acid Plants

TOLUENE

(TOLUOL)



From Coal Gas and Tar Light Oil



Yield

1 ton of coal yields about 0.5 gal toluene.

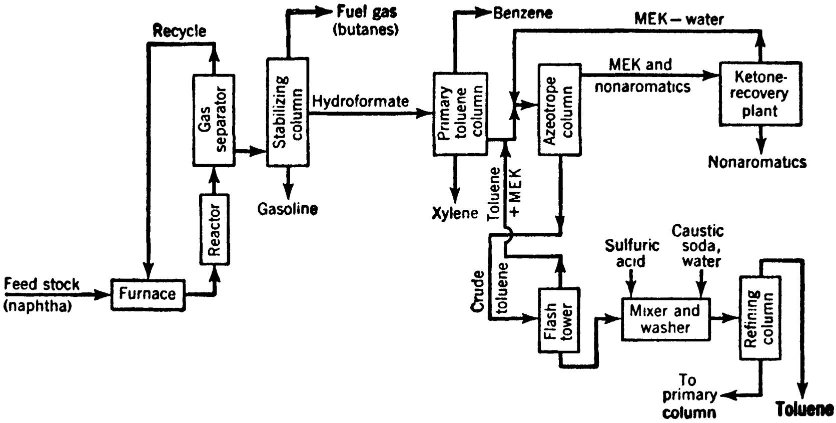
Process

Toluene or toluol (the crude product) is obtained from light oil by fractional distillation. The light oil, formed by coal carbonization (see *Coke*), is recovered by cooling and scrubbing the by-product coke-oven gas. The light oil, which condenses with the tars (about 5 per cent of the tar), is recovered by rectification. (See *Naphthalene* for coal-tar distillation and *Benzene* for light-oil distillation.)

The light oils (containing 12 to 20 per cent toluene), scrubbed from coke-oven gas and distilled from tar, are combined and fractionally distilled in continuous or semicontinuous units. Between 0.1 and 0.2 gal of toluene is obtained per gal of combined light-oil distilled. Generally, four fractions are taken in the crude distillation. The second cut, from about 95 to 125°C, consists of crude toluene which is sent to an acid-resistant agitator for washing. Here the crude toluene is treated with successive small portions of 66°Bé sulfuric acid to remove unsaturated compounds. Usually, between 0.3 and 0.7 lb of sulfuric acid is used in 4 to

6 portions per gal of oil. The toluene is treated with a sufficient quantity of 10 per cent sodium hydroxide solution to remove the free acid. The washed toluene is fractionally distilled in batch vacuum columns to yield refined toluene.

From Petroleum by Hydroforming



Reaction (Typical)

$$\underset{\text{Methyl cyclohexane}}{C_6H_{11}CH_3} \rightarrow \underset{\text{Toluene}}{C_6H_5CH_3} + 3H_2$$

80–90% conversion

Material Requirements

Basis—1 ton toluene

Naphtha feed stock	Widely variable, depending on feed stock
Sulfuric acid	
Caustic soda	
Methyl ethyl ketone	

Process

Toluene is produced from specially selected fractions of petroleum, rich in naphthenes, by a process known as hydroforming. This involves catalytic dehydrogenation in the presence of hydrogen (which reduces coke formation) to yield a mixture of aromatic hydrocarbons, chiefly toluene.

For the synthesis of toluene, the hydroformer raw material should be rich in dimethylcyclopentane, methylcyclohexane, and ethylcyclopentane (the three chief toluene "synthesis compounds"). Other naphthenes, such as cyclohexane and dimethylcyclohexane will yield benzene and xylene, respectively. The feed stock also contains paraffin hydrocarbons, of which normal heptane and dimethylhexane are typical. These compounds pass through the hydroformer essentially unchanged and consequently contaminate the toluene hydroformate.

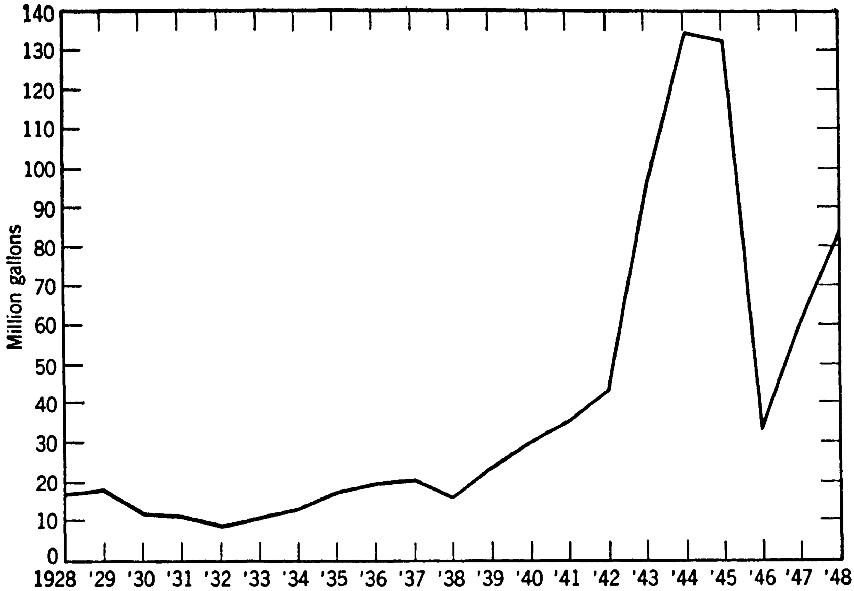
Crude petroleum and natural gasoline are processed by distillation to yield the hydroformer feed stock. For example, a California crude oil containing about 1.45 per cent synthesis hydrocarbons and 0.56 per cent natural toluene, is fractionally distilled, and a so-called heart cut is taken between 190 and 240°F. Natural and straight-run gasoline may also be processed by heart cutting to yield the maximum volume of feed stock obtainable.

The feed stock (a selected naphtha fraction) is preheated in heat exchangers and is then totally vaporized at 1,050°F in a furnace. Here it is joined with hydrogen-rich (70 per cent) recycle gas at 1,070°F, and the mixture is passed through a reactor with a contact time of about 15 sec. The reactor contains a dehydrogenation catalyst consisting of 10 per cent molybdenum dioxide on alumina. The reaction takes place at a temperature of 1,000 to 1,070°F, a pressure of 150 to 300 psi, and space velocity of 0.6 (volume of feed per hour divided by the volume of catalyst in the reactor). The ratio of recycle gas (70 per cent hydrogen) is about 6,000 cu ft per bbl of reactor charge (a barrel equals 42 gal in the petroleum industry).

The reaction gases pass through heat exchangers (preheating the feed stock) to a gas–liquid condenser and separator. Here a large portion of the separated wet gas is compressed (75 to 200 psi) and is recirculated to the furnace and reactor to increase the hydrogen concentration. The hydrogen tends to reduce coke deposition and thus maintain catalyst activity. The remaining gas and liquid pass to conventional absorption and stabilizing columns (fractionators), which produce fuel gas (butanes, etc.), gasoline, and hydroformate. The latter contains about 21 per cent toluene and may be recirculated through the reactor for maximum conversion to obtain a two-pass hydroformate containing 38 per cent toluene.

Two or more reactors are necessary for continuous operation because of the inactivating coke formation on the catalyst. One reactor is used for the dehydrogenation operation, while the second is being regenerated by burning with air or oxygen-containing flue gases. Generally, air is bled into an inert gas (mostly nitrogen and carbon dioxide) so that the mixture contains about 1.5 per cent oxygen. The latter combines with the coke, forming carbon dioxide and water, while the inert gas removes the heat of combustion. In passing through the catalyst bed the temperature is raised from 700° (inlet) to 1,100°F. The hot gases pass to waste heat boilers. The regenerated catalyst is reheated by hot flue gases, and then the inert gases, as well as water, are removed by purging with wet gas from the gas separators at atmospheric pressure.

The two-pass hydroformate (38 per cent toluene) is fed to the toluene-recovery plant where it is distilled. Three cuts are taken: the first, a benzene fraction and the last, a xylene fraction. See *Benzene* and *Xylene*, respectively. The heart cut, containing about 65 per cent toluene, is fed into an azeotropic distillation tower. If one-pass hydroformate (21 per cent toluene) is used, the heart cut contains about 39 per cent toluene. A mixture of methyl ethyl ketone (90 per cent) and water (10 per cent) is added to the azeotrope tower. This azeotrope loosely associates with the paraffins and naphthenes and carries them out the top of the tower to the ketone-recovery plant. The toluene, because of its higher-boiling point, moves down the tower and is removed from the bottom as crude toluene. The crude material is run to a column (flash tower), where the remaining methyl ethyl ketone plus some toluene is removed as the head cut. This fraction is returned to the azeotrope tower. The ketone-free toluene is then charged into a mixer, where it is washed with 98 per cent sulfuric acid (about 5 lb per bbl), settled, water-washed, and caustic-washed to remove small amounts of olefins. The



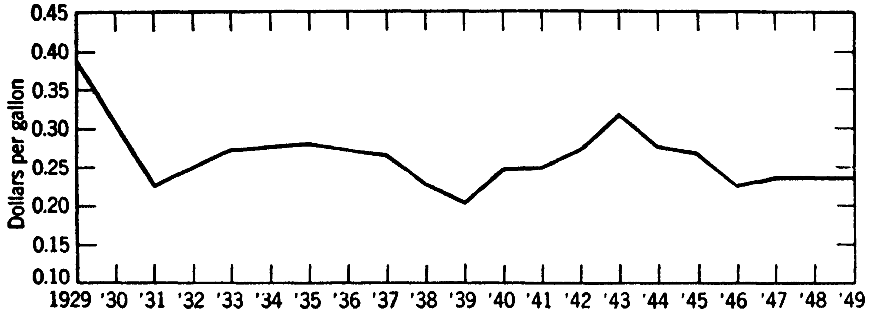
Production—Toluene (Crude and refined—not including ordnance plants) washed toluene is run to a refining column, where it is redistilled to produce nitration-grade toluene.

The methyl ethyl ketone recovery plant separates the ketone and nonaromatic hydrocarbons by countercurrent extraction with water. The ketone extract is separated from the water by distillation and is returned to the azeotrope tower. The nonaromatic raffinate from the water extraction is distilled to eliminate the water and ketone, leaving ketone-free nonaromatic hydrocarbons.

Use Pattern

	1944 (est.), per cent
Explosives and direct military	77
Aviation gasoline (including military)	17
Dyes	2
Protective coatings, solvents, and saturants	2
Miscellaneous	2
	100

In 1948 practically all 1 and 2° toluene was used as solvent; the unpurified concentrate from petroleum hydroformers was usually blended with aviation gasoline.



Price—Toluene

Miscellaneous

Properties. Colorless, refractory, flammable liquid with a benzene-like odor.

Mol. wt.	92.13	M.P.	−95.1°C
Sp. gr.	0.866 20°C/4	B.P.	110.8°C

Weight per gallon 7.21 lb (20°C)

Soluble in absolute alcohol, ether, acetone, and benzene. Insoluble in water (0.19 per cent at 20°C).

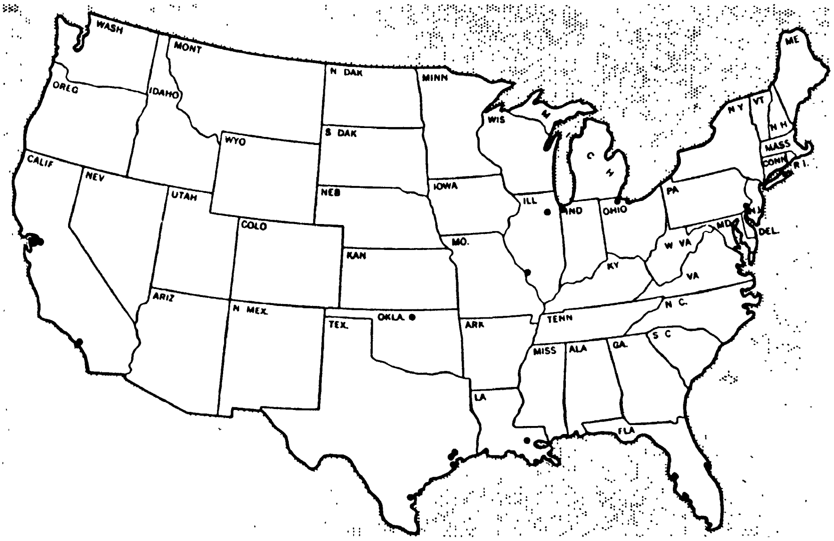
Flash point (closed cup)	40°F
Ignition temperature	1,026°F
Vapor density (air = 1)	3.14
Explosive limits (% by volume in air)	Lower 1.27 Upper 7.0

Grades. Nitration (2°), and industrial pure (1°).

Containers and Regulations. Tank cars, drums, pails, cans, and bottles. Red ICC shipping label required.

Economic Aspects

Most of the factors concerning by-product coke-oven plants previously discussed (see *Benzene*) are applicable also to toluene. Toluene, however, much more than benzene, is affected by wartime demands. In World War I, the coke and gas industries were able to recover sufficient toluene for TNT manufacture, but, during World War II, that effort would have been picayune. The Army Ordnance Department, therefore, turned to the petroleum industry and had built ten hydroforming and six recovery plants, with a total capacity of approximately 20,000,000 gal of toluene per month. Since the raw-material feed for recovery plants must contain toluene, the number of such plants is limited. The



Location of Synthetic-Toluene Plants

limit for hydroforming plants, on the other hand, has certainly not been reached. It was fortunate, however, that these plants could be converted readily to the manufacture of aviation gasoline, since peacetime demands for toluene are nowhere near plant capacity. It is not improbable that toluene produced in hydroformer plants will eventually have to supplement coke-oven benzene for nonchemical uses.

Hydroforming plants are understood to vary in size from 5,000,000 to 20,000,000 gal of nitration toluene per yr. Plants of this size cost $425 to $475 per 1,000 gal capacity. One hydroforming plant had a capacity of 70,000,000 gal of toluene per yr (twice prewar consumption) and cost considerably less per annual thousand gallons capacity.

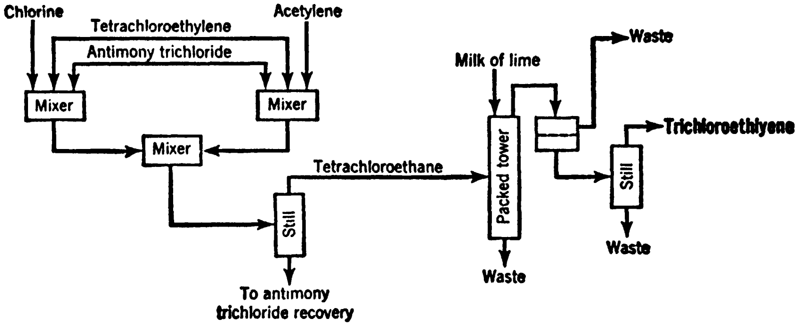
In case of emergency, additional recovery of toluene can be made by the coke and gas industries, by adding Bunker C oil to coal prior to coking, or by changing the operations in oil-gas sets.

Some toluene is obtained as a by-product in styrene manufacture (3 lb toluene per 100 lb styrene) (see *Styrene*).

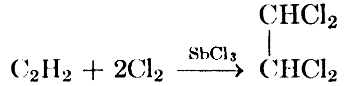
TRICHLOROETHYLENE

$ClHC{=}CCl_2$

From Acetylene and Chlorine



Reaction



$$C_2H_2 + 2Cl_2 \xrightarrow{SbCl_3} \begin{array}{c} CHCl_2 \\ | \\ CHCl_2 \end{array}$$

$$2CHCl_2{\cdot}CHCl_2 + Ca(OH)_2 \longrightarrow 2ClHC{=}CCl_2 + CaCl_2 + 2H_2O$$

90% yield

Material Requirements

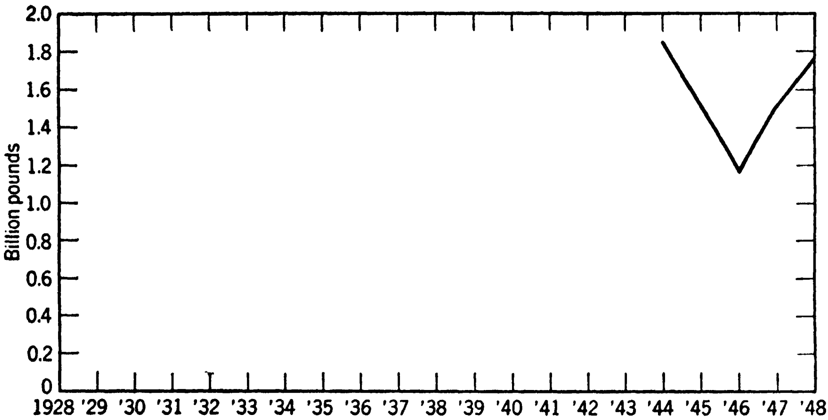
Basis—1 ton trichloroethylene

Acetylene	440 lb
Chlorine	2,400 lb
Lime (hydrate)	650 lb
Catalyst (loss)	Small

Process

Chlorine and acetylene are mixed independently, with either two separate mixtures or two separate portions of the same mixture of tetrachloroethane and antimony trichloride. These two mixtures, the one containing chlorine (60 to 80°C), and the other acetylene (80 to 100°C), are then brought into contact with each other under such conditions of efficient agitation and external cooling that high concentrations of neither chlorine nor acetylene contact each other. The actual design of equipment to carry out this reaction varies from plant to plant, but the fundamental design is obvious. The product, tetrachloroethane ($Cl_2HC \cdot CHCl_2$), is distilled from the reaction mixture and largely used for the manufacture of trichloroethylene, as follows:

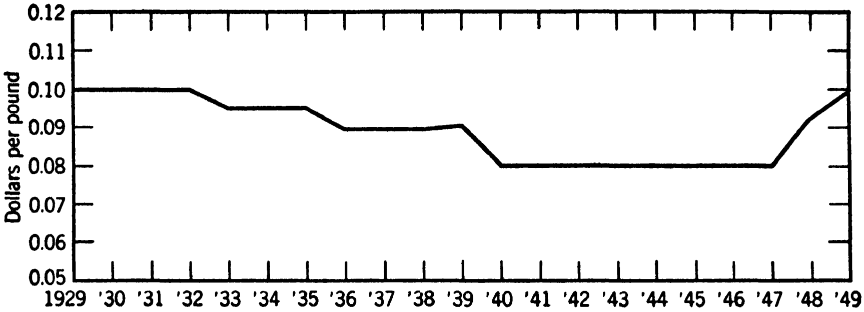
Tetrachloroethane is run countercurrently to a milk of lime suspension (10 per cent) in a heated packed tower, so operated that the temperature at the top of the tower (73°C) allows trichloroethylene to distil overhead; the temperature at the bottom (94°C) prevents loss of tetrachloroethane in the column effluent. The condensed trichloroethylene may be separated from water in a decanter and redistilled. The decanted distillate may be washed with caustic-soda solution prior to distillation.



Production—Halogenated Acyclic Hydrocarbons (No data available on trichloroethylene. For production data on chlorinated ethanes and ethylenes, see *Ethyl Chloride*)

Use Pattern

Degreasing and metal cleaning	>50 per cent
Dry cleaning Fat and oil extraction Heat exchange liquid Solvent	No breakdown available



Price—Trichloroethylene

Miscellaneous

Properties. Colorless, nonflammable, stable, heavy, toxic liquid with a characteristic, chloroform-like odor.

Mol. wt.	131.40	M.P.	−73°C
Sp. gr.	1.466 20°C/20	B.P.	87.2°C

Weight per gallon 12.20 lb (20°C)

Miscible with alcohol and ether in all proportions. Very slightly soluble in water (0.1 per cent at 20°C).

Grades. Technical (high purity).

Containers and Regulations. Tank cars, iron drums, cans, and bottles. Will not attack the common metals, even in the presence of moisture. No ICC shipping label required.

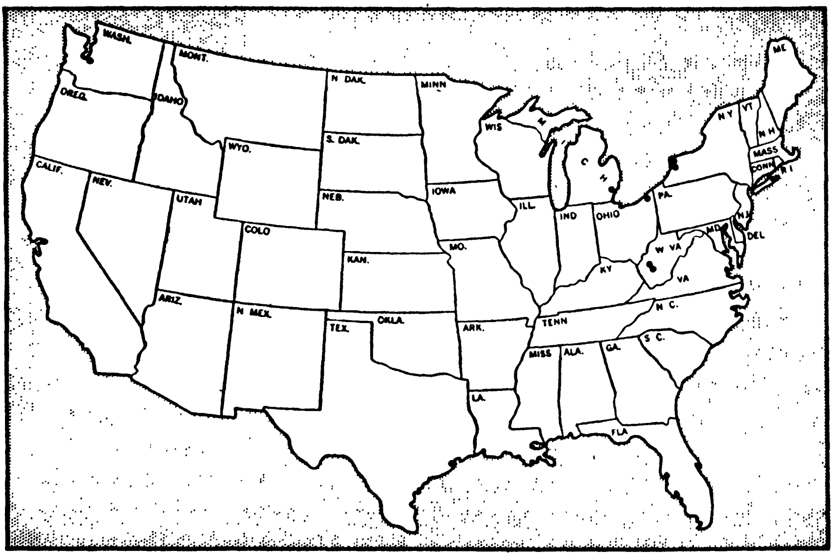
Economic Aspects

Trichloroethylene is one of a group of compounds (carbon tetrachloride, trichloroethylene, perchloroethylene, tetrachloroethane, and pentachloroethane) usually called chlorinated solvents. Before World War II, carbon tetrachloride was the most important of the group (see *Carbon Tetrachloride*), but, since that time, trichloroethylene has become the most important on a volume basis. Its great increase in use came during the war in the degreasing of metal machinery parts, in which field it was replacing carbon tetrachloride before the war. Further increase may be expected in the future because of the speed advantage (about four times) over alkaline cleaners in degreasing. In the dry-cleaning field, trichloroethylene is also expected partially to replace carbon tetrachloride. The latter is the cheaper of the two materials, but it also has a higher vapor pressure, which results in greater losses in many cleaning operations, and subsequent higher total cost.

Four of the chlorinated solvents listed previously (exception is carbon tetrachloride) may be manufactured in the same plant, in that tetrachloroethane (the original product of acetylene chlorination) may be converted to trichloroethylene which, in turn, may be converted to pentachloroethane by further chlorination, and the last-named product converted to perchloroethylene (tetrachloroethylene) by dehydrochlorination. Tetrachloroethane is also a by-product of the manufacture of ethyl chloride and ethylene dichloride and of the reduction of carbon tetrachloride. Cheap manufacture of trichloroethylene depends, of course, on a cheap source of the raw materials: acetylene and chlorine.

In certain dry-cleaning operations, the more expensive perchloroethylene is preferred to trichloroethylene, since it does not attack cellulose acetate dyes.

The usual size of a chlorinated-solvents plant will vary from 25,000,000 to over 100,000,000 lb annually. The cost of such plants is approximately $50 per 1,000 lb annual production. The present capacity of all trichloroethylene plants in the United States is about 250,000,000 lb per yr.



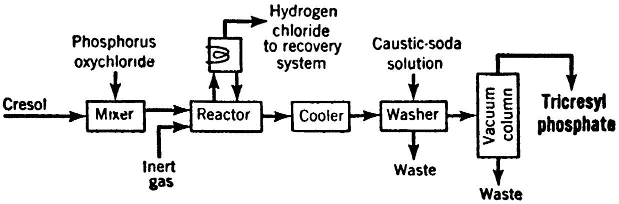
Location of Trichloroethylene Plants

TRICRESYL PHOSPHATE

(TRITOLYL PHOSPHATE)

$(CH_3C_6H_4O)_3PO$

From Cresol and Phosphorus Oxychloride



Reaction

$$3CH_3C_6H_4OH + POCl_3 \rightarrow (CH_3C_6H_4O)_3PO + 3HCl$$

85% yield

Material Requirements

Basis—1 ton tricresyl phosphate

Cresol	2,100 lb
Phosphorus oxychloride	980 lb

Process

Approximately chemically equivalent proportions of cresol and phosphorus oxychloride are blended together in a mixer. The more common grades of cresol used are the isomeric (*o*-, *m*-, *p*-) and meta–para mixtures from coal tar and cresylic acid from petroleum. The blended mixture is passed through a heat exchanger (70 to 140°C) to a reactor. The reactor generally consists of a direct-fired, airtight kettle connected to a suitable reflux condenser. If the reaction is carried out batchwise, the temperature of the reactor is slowly raised from about 150 to 300°C over a period of several hours. Hydrogen chloride gas is evolved and sent to a recovery system. At the end of the reaction (6 to 9 hr), the product is cooled and purified.

The reaction may be carried out in a continuous manner by having three or more reactors in series. If three reactors are used, the first one is maintained at a temperature of about 150°C, the second about 225°C, and the third about 300°C. The reactants flow slowly (by gravity) through each reactor (1 to 3 hr). Hydrogen chloride is evolved and passes through the reflux condensers to a recovery system. The removal of hydrogen chloride is generally facilitated by blowing the reaction mixture with an inert gas such as carbon dioxide or nitrogen, or by maintaining the reactor under vacuum.

The completely reacted materials from the last reactor are cooled in a heat exchanger and condenser and are led to purifiers. Here the crude tricresyl phosphate is treated to remove hydrochloric and phosphoric acids, free phenols, and other impurities. The method of refining depends on the end use of the product. The crude material may be washed with hot, dilute (2 per cent) sodium hydroxide solution and then water. This material is either packaged for sale (for lubricants and oil additives) or vacuum-distilled to give a refined grade of tricresyl phosphate. For the food wrapping and transparent plastic industries, the refined material may be treated with alkali permanganate, activated charcoal, or zinc and acid, to remove the last traces of cresol.

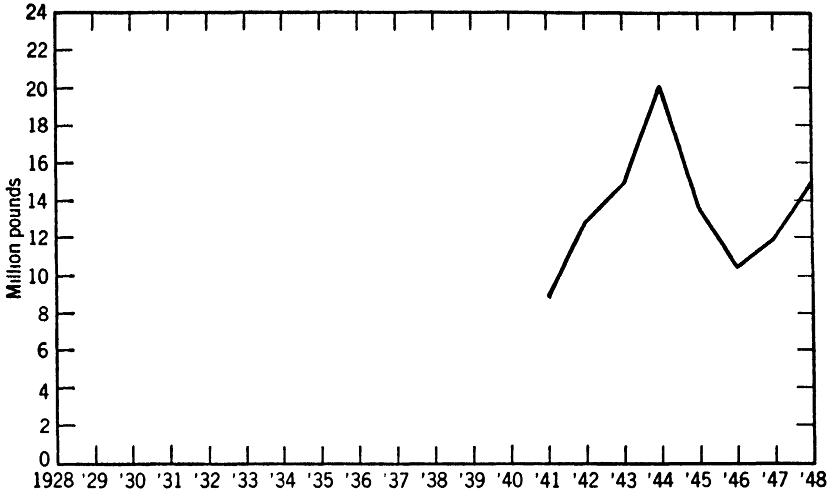
Tricresyl phosphate is generally obtained as a mixture of isomeric cresyl phosphates, depending on the nature of the cresol raw material. The yield of technical tricresyl phosphate based on cresol is approximately 88 per cent.

Phosphorus pentachloride may be used instead of the oxychloride to obtain tricresyl phosphate, according to the following equations:

$$3CH_3C_6H_4OH + PCl_5 \rightarrow (CH_3C_6H_4O)_3PCl_2 + 3HCl$$

$$(CH_3C_6H_4O)_3PCl_2 + H_2O \rightarrow (CH_3C_6H_4O)_3PO + 2HCl$$

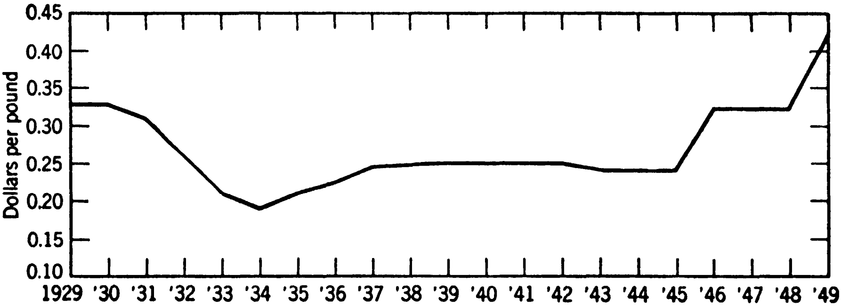
Cresol is charged into a reaction kettle, and phosphorus pentachloride is slowly added. The addition is continuous and at a rate of about 5 lb per min for a 900-lb cresol charge. Warm air containing a predetermined amount of moisture is blown into the bottom of the kettle. The heat for the reactor is supplied by the exothermic reaction. The temperature is maintained at approximately 80°C by adjustment of the rate of phosphorus pentachloride addition. When all the pentachloride has been added, the flow of moist air is continued until the hydrolysis reaction is completed. The hydrogen chloride evolved is removed in the air stream. The crude tricresyl phosphate is discharged from the reactor and purified as described previously. The yield is 85 to 90 per cent based on the weight of cresol charged.



Production—Tricresyl Phosphate

Use Pattern

	1947 (est.), per cent
Plasticizer	90
Miscellaneous, including lubricants and oil additives	10
	100



Price—Tricresyl Phosphate

Miscellaneous

Properties. Colorless to straw-yellow, stable nonvolatile oily liquid.

Mol. wt.	368.36	Congealing pt.	−20°C
Sp. gr.	1.165 20°C/20	B.P.	273–275 (17 mm)°C

Soluble in alcohol, ether, most common solvents and thinners, and vegetable oils. Insoluble in water.

Flash point (closed cup) 460°F

Grades. Technical, and C.P.

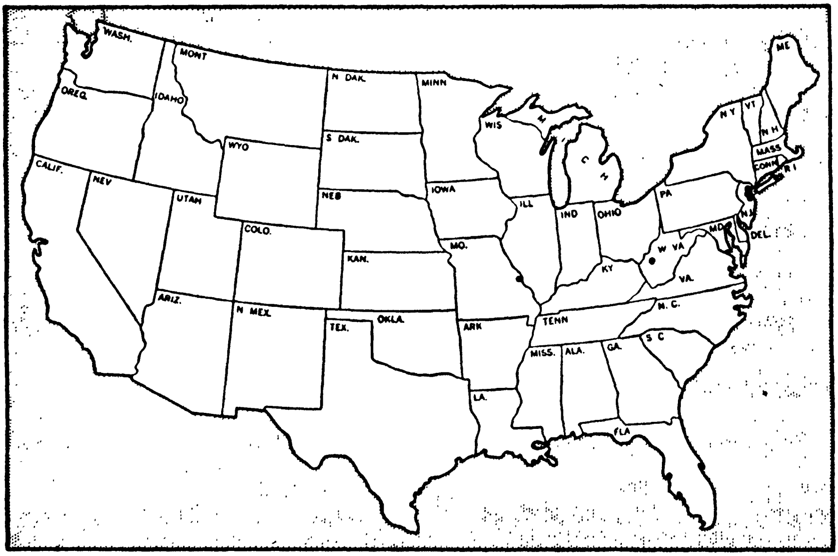
Containers and Regulations. Drums, cans, and bottles. No ICC shipping label required.

Economic Aspects

The value of tricresyl phosphate lies chiefly in its merit as a constituent of various lacquer films, coatings, and plastics. Its property of forming tough water-proof films led to greatly extended use during World War II as a cable coating. Its property of reducing the flammability of films has led to widespread use as a plasticizer for nitrocellulose. All the properties mentioned make tricresyl phosphate valuable also as a plasticizer for cellulose acetate and ethyl cellulose. As a volume plasticizer for vinyl plastics, it has no peer. There is little doubt that demand for this material and related plasticizers (triphenyl phosphate and tributyl phosphate) will increase rapidly.

Manufacture is much more difficult than a single flowsheet shows. The composition of the cresylic acid used (see *Cresol*) affects the properties of the ester and must be controlled. The ester must also be rigorously purified to separate free phenolic compounds, which not only give the product a bad odor but also make it corrosive.

Plant size usually varies from 2,000,000 to 5,000,000 lb annual capacity.

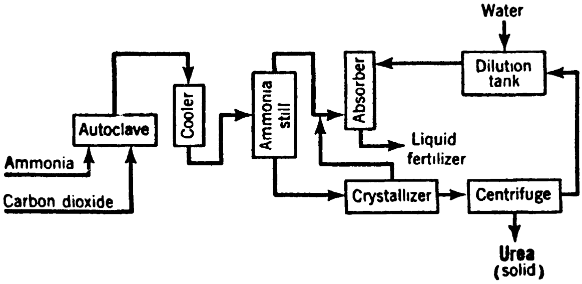


Location of Tricresyl Phosphate Plants

UREA

NH_2CONH_2

From Ammonia and Carbon Dioxide



Reaction

$$2NH_3 + CO_2 \rightarrow NH_2COONH_4 \rightarrow NH_2CONH_2 + H_2O$$

80% yield

Material Requirements

Basis—1 ton urea (60% solid, 40% liquid)

Ammonia	4,000 lb
Carbon dioxide	1,800 lb

Process

Urea is produced by the indirect dehydration of the intermediate, ammonium carbamate, formed by the high-pressure reaction of excess ammonia and carbon dioxide.

Ammonia and carbon dioxide, in a weight ratio of about 2.3 to 1 (3-to-1 mole ratio), are compressed (to liquids) and charged separately into a steam-heated, silver-lined autoclave (reactor). The reactants require about 2 hr to pass through the autoclave, which is maintained at a temperature of approximately 190°C and a pressure of 1,500 to 3,000 psi. During this time the ammonia and carbon dioxide react to form ammonium carbamate, which is largely converted to urea.

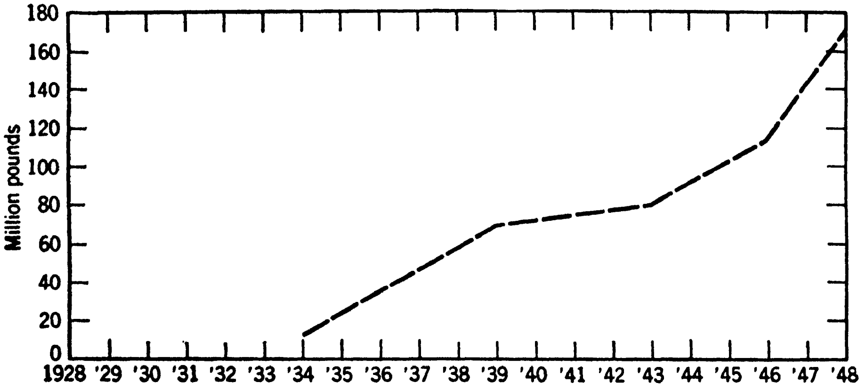
The reaction mixture, consisting of about 35 per cent urea, 8 per cent ammonium carbamate, 10.5 per cent water, and 46.5 per cent unreacted ammonia, is discharged from the autoclave and cooled to approximately 150°C. The melt is passed to an ammonia still, operating at 60°C, where 60 to 65 per cent of the unconverted ammonia and any unreacted carbon dioxide are distilled and collected in an ammonia-absorption system. The absorbed materials may be re-used in the reactor or converted to liquid fertilizer.

The residue in the ammonia still, consisting largely of urea and water, is discharged to a crystallizer where it is cooled to about 15°C. About 70 per cent of the remaining free ammonia is removed by vacuum and sent to the recovery system. The resulting slurry is passed to a continuous centrifuge, separating the crystalline urea. The mother liquor, containing about 21 per cent ammonium carbamate, 38 per cent urea, 14 per cent ammonia, and 27 per cent water, is sent to the ammonia-recovery system, where it is utilized in the manufacture of the liquid fertilizer.

The yield of urea in the crude melt based on the carbon dioxide charged is 80 to 85 per cent. If the ammonia recovered by absorption is taken into account, this yield is essentially the same based on the ammonia charged. However, about 60 per cent of this crude urea is recovered as crystalline product, the remainder going to make up liquid fertilizer (urea–ammonia liquor).

From Calcium Cyanamide

Urea may also be produced by the action of carbon dioxide on calcium cyanamide suspended in water. Free cyanamide and calcium carbonate are formed. The acid hydrolysis of the free cyanamide yields urea,



Production—Urea (Estimated)

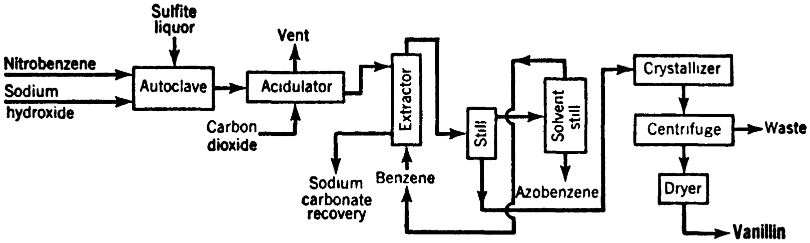
The two principal uses for urea (plastics and fertilizer) appear to offer promise of much greater utilization in the future. Urea–formaldehyde plastics are particularly well-appearing and may be fabricated in a wide variety of bright colors. In the fertilizer field, the ammoniation of superphosphate with urea–ammonia liquor (urea dissolved in liquid ammonia) is headed for much greater use. A small amount of urea is used as a stabilizer in smokeless powder. Recently, increasing amounts have been added to animal feeds as a protein replacement. The potentialities of this use are said to be tremendous.

One commercial urea plant is said to have a capacity of 170 tons per day (60,000 tons per year). The smallest economic-sized plant should have a capacity of at least 10 tons per day (3,000 to 3,500 tons annually).

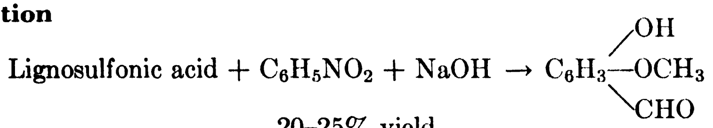
VANILLIN

$(HO)(CH_3O)C_6H_3CHO$

From Waste Sulfite Pulp Liquor



Reaction



$$\text{Lignosulfonic acid} + C_6H_5NO_2 + NaOH \rightarrow C_6H_3\begin{cases} OH \\ OCH_3 \\ CHO \end{cases}$$

20–25% yield

Material Requirements

Basis—100 lb vanillin

Sulfite-liquor solids	1,150 lb
Sodium hydroxide	1,350 lb
Nitrobenzene	1,350 lb
Carbon dioxide	825 lb
Benzene (make-up)	25 lb

Process

Vanillin is obtained by oxidizing lignin-containing substances such as waste sulfite pulp liquor.

Waste sulfite liquor, containing about 15 per cent sulfite solids (mainly lignosulfonic acid) is charged to a closed pressure kettle. Approximately equal weights of nitrobenzene and sodium hydroxide are added to the liquor so that a nitrobenzene–sodium hydroxide–sulfite solids ratio of 1.2 to 1.2 to 1 results. The mixture is heated to 200°C and allowed to digest for about 1 hr.

The pressure is released, and the reaction liquor is discharged into an acidulator, into which carbon dioxide in excess is bubbled. Generally, a small amount of sulfuric acid is added to complete the acidification.

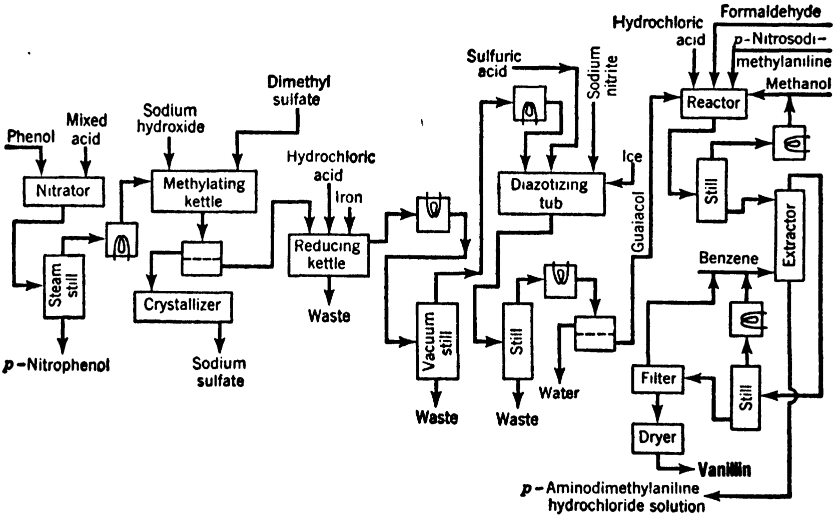
The mixture is then run into an extractor, where the free vanillin is extracted with benzene. The lower water layer, containing sodium bicarbonate, sodium sulfite, sodium sulfate, lignin, and related substances, is run either to waste or to recovery units. Here, sodium carbonate may be recovered by treatment to remove insoluble calcium salts, followed by drying and incineration.

The top (benzene) layer, containing vanillin, azobenzene, and similar reaction products, is charged into a still, where the volatile solvents are distilled and recovered. About an 80 per cent recovery of azobenzene is realized based on the amount of nitrobenzene charged. The crude vanillin residue is steam-distilled and then crystallized to give purified vanillin. Yields of 8 to 15 per cent based on dry sulfite solids are realized.

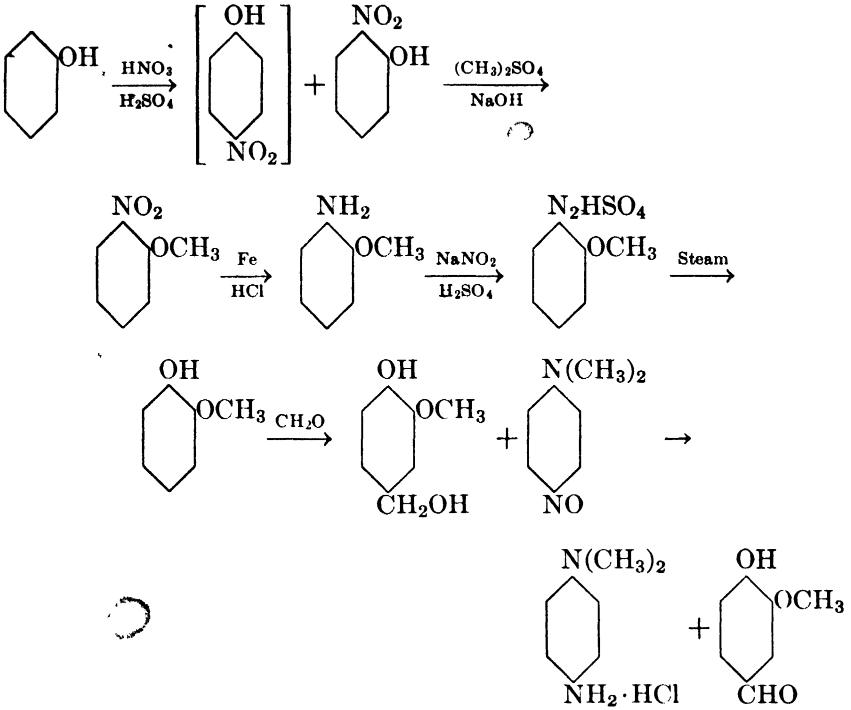
The use of air instead of nitrobenzene as an oxidizing agent is claimed in a recent patent. By operating below 170°C in this manner, vanillin yields are said to be increased by 60 to 80 per cent.

Vanillin may also be produced by the alkaline hydrolysis of lignosulfonic acid. A yield of about 8 per cent is obtained, using a process similar to the afore-mentioned. Generally hydrated lime is added to the sulfite waste liquor to precipitate calcium lignosulfonic acid, which serves as the raw material. The calcium lignosulfate is hydrolyzed to vanillin under pressure with a strong caustic-soda solution, and the resulting sodium salt of vanillin is extracted with butanol. Recent work has indicated that ion-exchange resins may be useful in recovering vanillin from dilute solutions.

From Phenol through Guaiacol



Reaction



20% yield

Material Requirements

Basis—100 lb vanillin
(plus 145 lb *p*-nitrophenol and 150 lb *p*-aminodimethylaniline hydrochloride)

Phenol	310 lb	Sulfuric acid (41°Bé)	215 lb
Mixed acid ($H_2SO_4+HNO_3$)	1,175 lb	Formaldehyde	38 lb
Dimethyl sulfate	64 lb	*p*-Nitrosodimethylaniline	180 lb
Sodium hydroxide	575 lb	Benzene	23 lb
Iron	20 lb	Methanol	23 lb
Hydrochloric acid	23 lb	Steam	1,540 lb
Sodium nitrite	55 lb		

Process

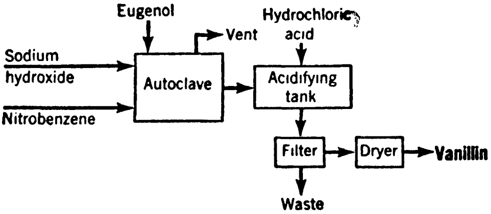
Vanillin may be made synthetically from guaiacol by reaction with formaldehyde, *p*-nitrosodimethylaniline, and hydrochloric acid. Guaiacol may be obtained directly from wood tar produced by the destructive distillation of hardwood or by fractionation of the phenol fraction of coal tar. It is also produced synthetically from phenol as follows:

Phenol is charged into a nitrator, and mixed nitrating acid (60 per cent sulfuric acid, 32 per cent nitric acid, and 8 per cent water) is added. The nitrated reaction product is discharged into a steam still, where the orthonitro isomer is separated from *p*-nitrophenol.

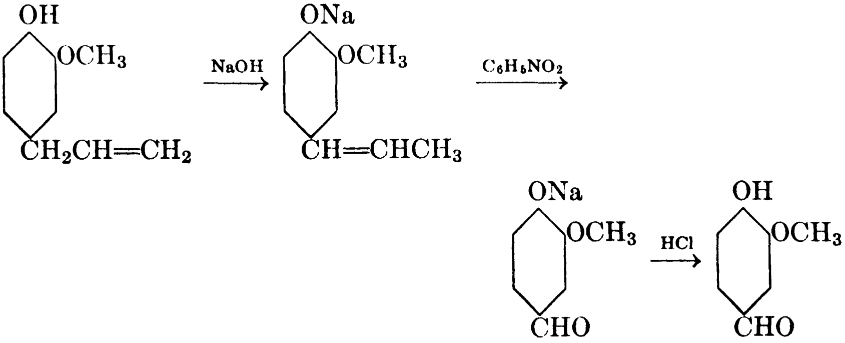
An alternate method starts with *o*-nitrochlorobenzene which is hydrolyzed to *o*-nitrophenol.

Orthonitrophenol is run into a kettle where it is methylated with dimethylsulfate in the presence of sodium hydroxide. The reaction product is separated into sodium sulfate and *o*-nitroanisole. The latter is reduced with iron and hydrochloric acid, and, after vacuum distillation, *o*-aminoanisole is diazotized with sodium nitrate and sulfuric acid. The diazo compound is steam-distilled to yield guaiacol which, after separation by decantation from water, is reacted for 2 hr with 4 parts of 37 per cent formaldehyde and 4 parts of *p*-nitrosodimethylaniline in the presence of 12 parts of methanol poured into water and hydrochloric acid. The methanol is stripped from the reaction product, which is extracted with benzene. The water layer contains *p*-aminodimethylaniline hydrochloride, whereas the extract contains vanillin. The benzene is removed, and the vanillin is filtered and dried.

From Eugenol



Reaction



80% yield

Material Requirements

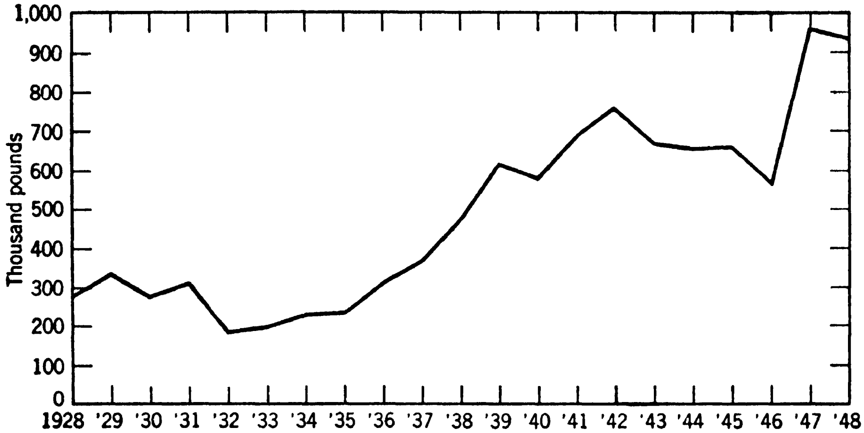
Basis—100 lb vanillin

Eugenol	135 lb
Sodium hydroxide	55 lb
Nitrobenzene	100 lb
Hydrochloric acid (20°Bé)	160 lb

Process

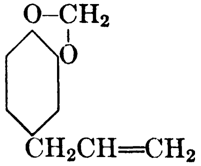
Eugenol, obtained from oil of cloves, is converted to isoeugenol by heating with an alkali. The latter is then oxidized to yield vanillin.

Oil of cloves and cinnamon-leaf oil contain up to 90 per cent eugenol. To extract it, the oils are treated with alkali; the aqueous solution is separated and acidified with dilute acid; and the resulting eugenol is washed and fractionated. The eugenol is dissolved in dilute sodium hydroxide solution and charged into an autoclave. After heating at 160°C under pressure, the sodium salt of isoeugenol is formed. The reaction product is cooled slightly, and 1 mole of nitrobenzene is added per mole of eugenol originally present. The slow addition under pressure controls the oxidation. After the reaction is complete, the pressure in the autoclave is released and the gaseous by-products are vented.



Production—Vanillin

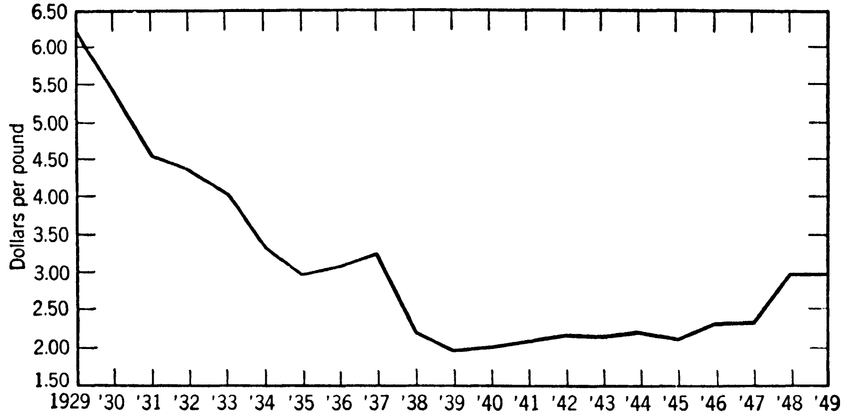
The reaction mass is discharged into an acidulator, where it is treated with hydrochloric acid to yield vanillin. The crystals are filtered and washed and may be purified by recrystallization. The yield of vanillin is about 80 per cent of theory.

Vanillin has been produced from safrole, 

(obtained from camphor oil) by treatment with alkali to give isosafrole. After conversion to protocatechuic aldehyde, methylation gives vanillin.

Use Pattern

Flavoring agent 100 per cent



Price—Vanillin

Miscellaneous

Properties. White crystalline needles with a pleasant aromatic odor and a vanilla taste.

Mol. wt.	152.14	M.P.	81-82°C
Sp. gr.	1.056	B.P.	285 (in CO_2)°C

Soluble in alcohol, ether, chloroform, glycerine, carbon disulfide. Slightly soluble in water (1 per cent at 14°C, 5 per cent at 75°C).

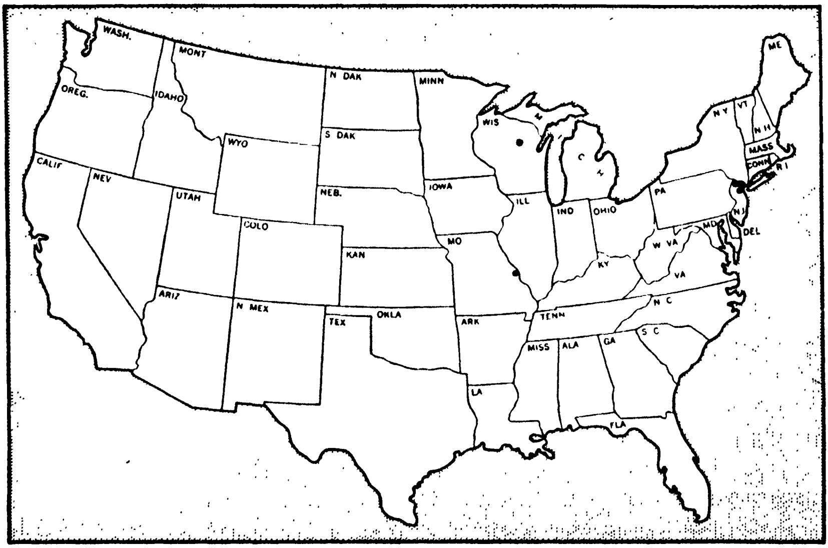
Grades. Technical, and USP.

Containers and Regulations. Drums, tins, and bottles. No ICC shipping label required.

Economic Aspects

Vanillin is one of the most important of the synthetic flavoring materials in terms of the quantity used, the others being methyl salicylate (wintergreen) and terpineol. Three synthetic processes are important: that is, from eugenol, guaiacol, and lignin. A fourth, starting with isosafrole, is less important. The eugenol and guaiacol processes have been competitive for years, but the lignin process has led to much lower prices and promises to supplant the older processes. Synthetic vanillin must compete, of course, with natural vanilla, extracted from the vanilla bean. Although the flavor of natural vanilla is due primarily to vanillin (the beans contain 2 to 3 per cent), some of the flavor results from resins and other ingredients extracted from the bean. In one way this works to the advantage of the synthetic product, since no two lots of natural vanilla have identical flavor. On the other hand, the preference of users for vanillin made from a particular raw material, or blended in a certain way, complicates marketing. In early 1950 vanillin from eugenol was quoted at $4 per pound, whereas that from lignin and from guaiacol was quoted at $3 per pound. Some users prefer a blend of the natural and synthetic products; others prefer vanillin blended with coumarin, or even ethyl vanillin blended with coumarin.

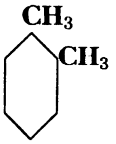
The economic plant size of the older processes is quite small, but this is of no avail if the processes are obsolete, as they may well be. The lignin process is of such a nature that the most economic plant could probably supply the entire American demand. Vanillin manufacture does not appear attractive to new producers with the present market. New and larger uses in synthesis could change the situation.



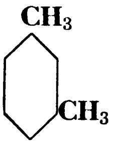
Location of Vanillin Plants

XYLENE

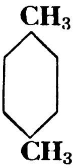
(XYLOL)



ortho-

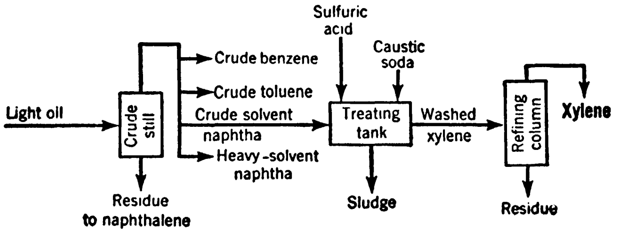


meta-



para-

From Coal Gas and Tar Light Oil



Yield

1 ton of coal yields about 0.3 gal xylene.

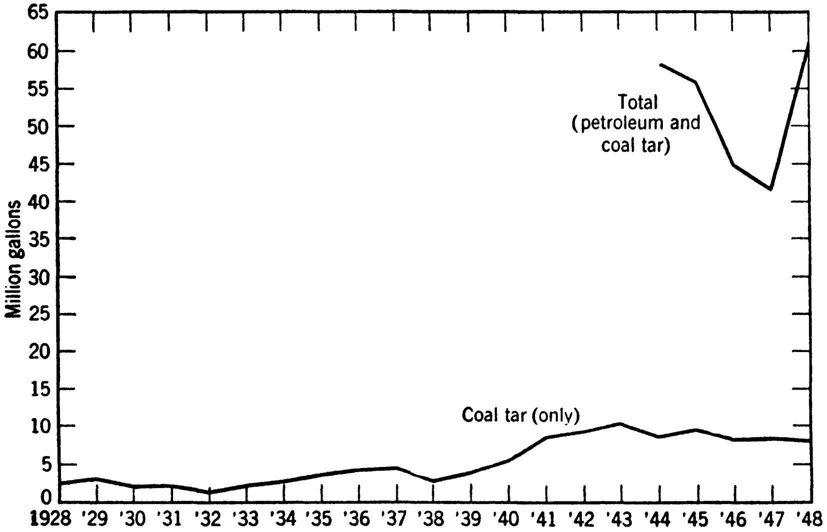
Process

Xylene or xylol (the crude product) is obtained from light oil in a manner similar to that described for benzene and toluene. Light oil, formed by the high-temperature carbonization of coal (see *Coke*), is recovered by condensing and scrubbing the coal gas. The oil that condenses with the tar is recovered by distillation (see *Naphthalene*). The light oil from the gas scrubbers (see *Coke*) and the tar light oil are combined and sent to the refinery (see *Benzene*).

The light oil, containing 4 to 7 per cent xylene (chiefly the meta isomer), is distilled to yield several fractions. The third cut, called crude light solvent, constitutes 4 to 8 per cent of the original crude and consists mainly of the three isomeric xylenes, ethylbenzene, and styrene. The yield of aromatic hydrocarbons from this fraction is 65 to 75 per cent, while the "unsaturates" (including styrene) range from 20 to 25 per cent. The crude xylol (light-solvent naphtha) is treated with sulfuric acid to remove the unsaturated compounds. After neutralization with caustic soda and water, the washed xylol is refined by batch distillation (see *Benzene* and *Toluene* for washing and distillation details).

The refined product (industrial xylol) is a mixture of hydrocarbons as follows: 68 to 70 per cent *m*-xylene, 18 to 19 per cent *p*-xylene, 3 to 5 per cent *o*-xylene, and 7 to 9 per cent ethylbenzene. The grades of xylene depend on the sharpness of fractionation. The fraction taken from the pure stills is generally called refined light solvent or industrial xylol. Closer fractionation results in 10° xylol, 5° xylol, and nitration or pure xylol. The separation of the pure xylene isomers is not practiced on a commercial scale.

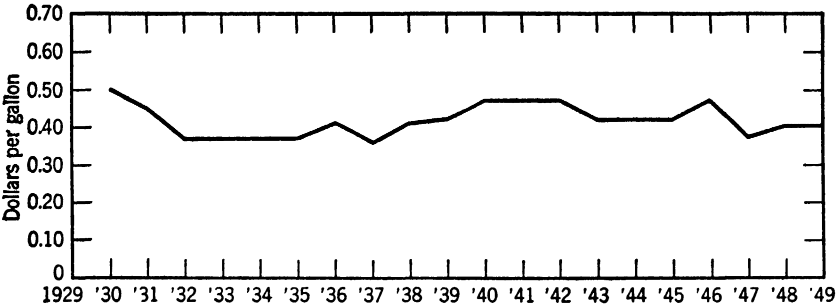
Xylene is also obtained from certain petroleum fractions by hydroforming. See *Toluene* for details. The xylene fraction that is separated from the hydroformate may be sold as such or may be further purified. Orthoxylene for phthalic anhydride manufacture may be obtained by the fractional distillation of the isomeric mixture. A distillate, rich in *m*- and *p*-xylene, is obtained leaving a residue of 85 to 90 per cent *o*-xylene.



Production—Xylene (Crude)

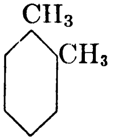
Use Pattern

Protective coatings	No breakdown available
Gasoline blends	
Phthalic anhydride	
Xylidines	
Miscellaneous	



Price—Xylene (3-degree)

Miscellaneous

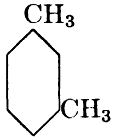
Properties. *o-Xylene,*  Clear, colorless, toxic flammable liquid with a characteristic odor

Mol. wt.	106.16	M.P.	−25°C
Sp. gr.	0.881 20°C/4	B.P.	144°C

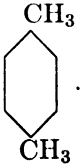
Weight per gallon 7.3 lb (20°C)

Soluble in alcohol and ether. Insoluble in water.

Flash point (closed cup)	63°F
Ignition temperature	900°F
Vapor density (air = 1)	3.66
Explosive limits (% by volume in air)	Lower 1.0 Upper 5.3

m-Xylene,  Colorless liquid.

Mol. wt.	106.16	M.P.	−47.4°C
Sp. gr.	0.867 17°C/4	B.P.	139.3°C

p-Xylene,  . Colorless crystals (plates) or liquid.

Mol. wt.	106.16	M.P.	13.2°C
Sp. gr.	0.861 20°C/4	B.P.	138.5°C

Grades. Nitration xylol (3° distillation range), 5° xylol, 10° xylol, industrial xylol (90 per cent distils below 150°C, all below 160°C).

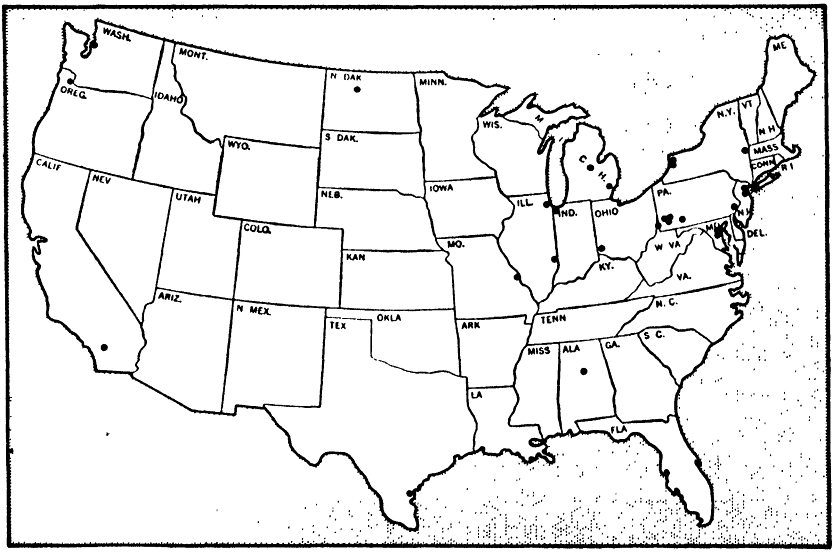
Containers and Regulations. Tank cars, drums, pails, cans, and bottles. Red ICC shipping label required.

Economic Aspects

Methods of producing xylene follow closely those used for toluene (see *Toluene*, also *Benzene*). Light oil contains only about 5 per cent xylene, and quite often it is not recovered in pure form. During the war, a few hydroformers were run on various petroleum stocks to supply xylene as a raw material for mixed xylidine manufacture. This latter product was used as an additive in aviation fuels for rich mixture performance. Any new large requirements for xylene will also have to be furnished by the petroleum industry.

The only recent new large-scale use for xylene has been in phthalic anhydride manufacture (see *Phthalic Anhydride*). Here xylene is fractionated to give *o*-xylene as the raw material, and the meta-para fraction is used in motor fuel. As terephthalic acid becomes more important industrially, there may be an increased demand for *p*-xylene.

In a few cases, cyclopentadiene is recovered as a by-product from the forerunnings of xylene distillation. Some thought has been given to the recovery of carbon disulfide and olefins, also present in the forerunnings.



Location of By-Product Toluene and Xylene Plants

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